An efficient dehydroxymethylation reaction by a palladium catalyst†

Atanu Modak, Togati Naveen and DebabrataMaiti*

Department of Chemistry, Indian Institute of Technology Bombay,
Powai, Mumbai 400076

RECEIVED DATE (automatically inserted by publisher); E–mail: dmaiti@chem.iitb.ac.in

Supporting Information

General considerations:

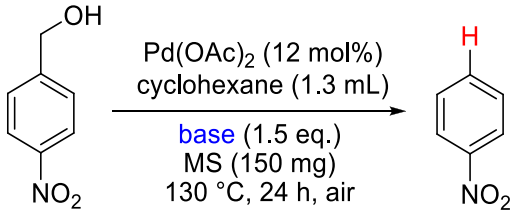
Reagent information. Unless otherwise stated, all reactions were carried out under air in screw cap reaction tubes. All the solvents were bought from Aldrich in sure seal bottle and were used as received. Palladium catalysts were obtained as gift from Johnson Matthey Chemicals, MIDC Taloja, India and ligands were purchased from Aldrich and Merck. Moleculer sieves (4Å; particle size 2–3 μ) were bought from Aldrich. Anhydrous Na_2CO_3 was purchased from Fisher Scientific. Moleculer sieves and anhydrous Na_2CO_3 were always kept in oven in small amount before use. All primary alcohols were bought from Aldrich. For column chromatography, silica gel (60–120 mesh or 100–200 mesh) from SRL Co. was used. A gradient elution-using pet–ether and ethyl acetate was performed, based on Merck aluminium TLC sheets (silica gel $60F_{254)}$.

Analytical Information. All isolated compounds were characterized by ^{1}H NMR, ^{13}C NMR spectroscopy, melting point and
gas chromatography mass spectra (GC–MS). Copies of the ^{1}H NMR, ^{13}C NMR can be found in the Supporting Information. Unless otherwise stated, all Nuclear

Magnetic Resonance spectra were recorded on a Bruker 400 MHz instrument. Some Nuclear Magnetic Resonance was taken on a VARIAN 400MHz instrument. All ^{1}H NMR experiments were reported in units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent, unless otherwise stated. All ^{13}C NMR spectra were reported in ppm relative to deuterochloroform (77.23 ppm), unless otherwise stated, and all were obtained with ^{1}H decoupling. All GC analyses were performed on a Agilent 7890A GC system with an FID detector using a J & W DB–1 column (10 m, 0.1 mm I.D.). All GCMS analysis was done by Agilent 7890A GC system connected with 5975C inert XL EI/CI MSD (with triple axis detector). High-resolution mass spectra(HRMS) were recorded on a micromass ESI TOF (time of flight) mass spectrometer.

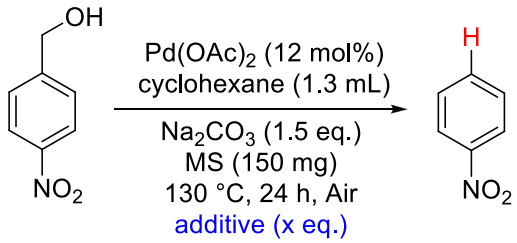
Optimization details for palladium catalyzed dehydroxymethylation:

(i) Optimization by varying base:



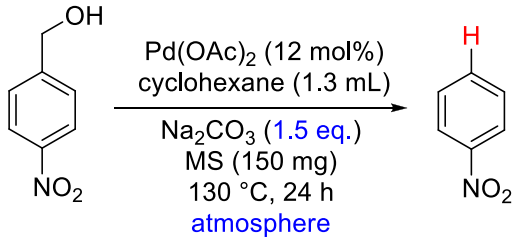
Entry	Base	GC Yield (%)
1	Na_2CO_3	62
2	K_2CO_3	62
3	K_3PO_4	34
4	Cs_2CO_3	42
5	KO^tBu	0
6	NaOAc	25
7	Et_3N	7
8	Pyridine	28
9	DABCO	52
10	DBU	2
11	2-6 Lutidine	11
12	Hunig Base	15
13	-	30

(ii) Optimization by varying additives (type and amount):



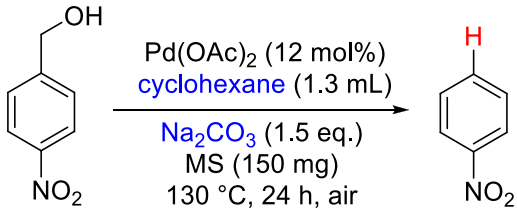
Entry	Additive	Amount (eq.)	GC Yield (%)
1	-	-	67
2	Pyridine	0.1	66
3	Pyridine	0.4	48
4	Pyridine	0.6	60
5	Benzoquinone	1	2
6	Benzoquinone	1.5	1

(iii) Optimization by varying atmosphere of reaction and base amount:



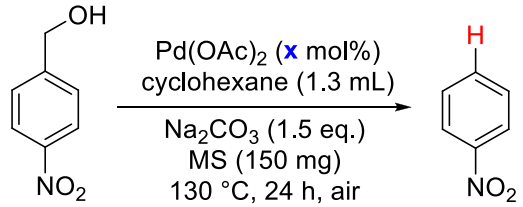
Entry	Atmosphere	Base (eq.)	GC Yield (%)
1	Oxygen	-	17
2	Oxygen	1.5	57
3	Air	0.5	37
4	Air	1.5	59
5	Air	2.5	58
6	Air	3.5	59

(iv) Optimization by varying type of solvent and base amount:



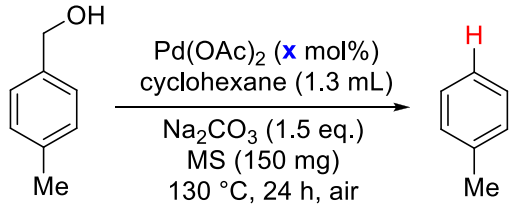
Entry	Cyclohexane	Na_2CO_3 (eq.)	GC Yield (%)
1	Normal	1.5	60
2	O_2 purged	1.5	57
3	Normal	-	30
4	O_2 purged	-	30

(v) Optimization by varying catalyst loading:

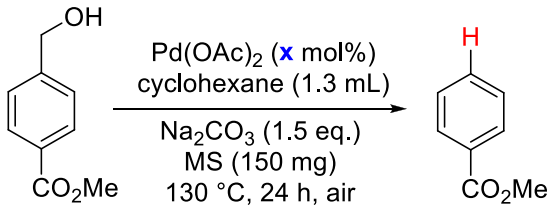


Entry	Catalyst (mol %)	GC Yield (%)
1	8	61
2	10	66
3	12	80 (73*)

**isolated yield*

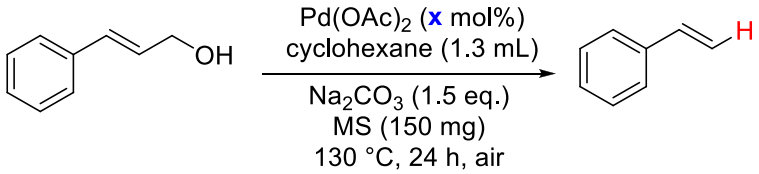


Entry	Catalyst (mol %)	GC Yield (%)
1	8	52
2	12	54
3	16	68
4	16 (48 h)	85



Entry	Catalyst (mol %)	GC Yield (%)
1	10	66
2	12	72
3	12 (36 h)	83*

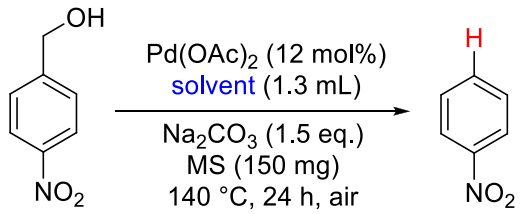
**isolated yield*



Entry	Catalyst (mol %)	GC Yield (%)
1	10	56
2	12	63*

**isolated yield*

(vi) Optimization by varying solvent:



Entry	Solvent	GC Yield (%)
1	Cyclohexane	57
2	Dichloroethane(DCE)	37
3	2-Methyltetrahydrofuran	15
4	Dioxane	1
5	Benzene	38
6	Chloroform	0
7	Anisole	1
8	TFT	27
9	DMF	50
10	Ethylcyclohexane	58

General Procedure A for dehydroxymethylation of primary alcohols

A clean, oven–dried screw cap schlenk reaction tube with previously placed magnetic stir–bar was charged with molecular sieves (4Å, 150 mg); primary alcohol (0.5 mmol); Na_2CO_3 (1.5 eq., 0.75 mmol, 79 mg); palladium acetate (12-16 mol%). Cyclohexane (1.5mL)/ethylcyclohexane (2 mL) was added to this mixture by syringe. The tube was tightly closed by screw cap and placed in a preheated oil bath at 130 °C. The reaction mixture was vigorously stirred for 24-36 h. The reaction mixture was cooled to room temperature and filtered through celite. Reaction tube and residue was washed with ethyl acetate (20 mL). The filtrate was concentrated and resulting dehydroxymethylated product was purified via column chromatography using silica gel and pet ether- ethyl acetate as eluate.

Fig. 1. Pictorial description of reaction tube for dehydroxymethylation: Fisherbrand Disposable Borosilicate Glass Tubes (16*125mm) with Threaded End (Fisher Scientific Order No. 1495935A) [left]; Kimble Black Phenolic Screw Thread Closures with Open Tops (Fisher Scientific Order No. 033407E) [middle]; Thermo Scientific National PTFE/Silicone Septa for Sample Screw Thread Caps (Fisher Scientific Order No. 03394A) [right].

General Procedure B for reduction of aldehyde to primary alcohol

Aldehyde was taken in a clean round bottom flask, charged with magnetic stir bar. Ethanol was added to dissolve the aldehyde and placed on a magnetic stirrer. $NaBH_4$ (1.5 eq.) was added to this solution in portion-wise with constant stirring at room temperature. Reaction mixture was stirred at room temperature for complete conversion (checking by TLC). The remaining ethanol was removed in rota-vap. Then water was added to this reaction mixture and organic part was extracted by diethyl ether and dried over anhydrous Na_2SO_4. Organic part was concentrated and primary alcohol was purified through silica gel (60-120 mesh) using pet ether – ethyl acetate mixture as eluent.

General Procedure C for preparation of starting materials by C–N Coupling[1]

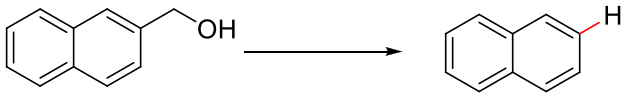
In an oven dried schlenk reaction tube, charged with magnetic stir bar *p*–tolyl iodide (1.5 mmol); CuI (20 mol%, 0.3 mmol, 57 mg); heterocyclic aldehyde (1.5 mmol); 1,10–phenanthrolene (40 mol%, 0.6 mmol, 119 mg) and base (3 mmol) were added. Then the reaction tube was evacuated and back filled with nitrogen. This vacuum/ nitrogen sequence was repeated for four times. Toluene (3 mL) was added under the positive pressure of nitrogen and the resealed tube was immersed in a preheated oil bath at 130 ºC and stirred vigorously for 24 hours. The reaction mixture was cooled to room temperature, diluted with 5 mL ethyl acetate and filtered through celite using additional 10 mL ethyl acetate. The filtrate was concentrated and purified by column chromatography (100–200 mesh) eluting with pet ether–ethyl acetate mixture.

General Procedure D for preparation of starting materials by C–C Coupling[2]

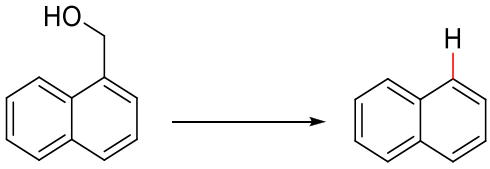
In an oven dried schlenk reaction tube, charged with magnetic stir bar *p*–bromobenzaldehyde (1 mmol); $Pd(OAc)_2$ (1.5 mol%, 0.015 mmol, 4 mg); boronic acid (1.1 mmol); X-phos (3 mol%, 0.03 mmol, 14 mg) and $K_3PO_4.H_2O$ (3 eq., 3 mmol, 690mg) were added. Then the reaction tube was evacuated and back filled with nitrogen. This vacuum/ nitrogen sequence was repeated for four times. Dry THF (3 mL) was added under the positive pressure of nitrogen and the resealed tube was immersed in a preheated oil bath at 100 ºC and stirred vigorously for 24 hours. The reaction mixture was cooled to room temperature, diluted with 5 mL ethyl acetate and filtered through celite using additional 10 mL ethyl acetate. The filtrate was concentrated and purified by column chromatography (100–200 mesh) eluting with pet ether–ethyl acetate mixture.

General Procedure E for preparation of starting materials by Cu catalyzed C–O Coupling [3]

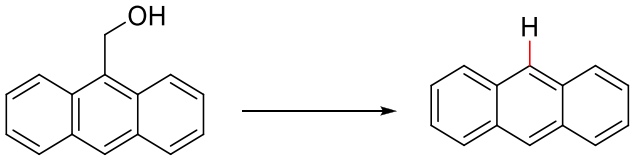
Aryl phenol (2.5 mmol), CuI (5 mol%, 0.125 mmol, 24 mg), picolinic acid (20 mol%, 0.25 mmol, 31 mg), K_3PO_4 (2 eq., 5 mmol, 1.060 gm), arylbromide (3 mmol) were taken in an oven dried schlenk reaction tube, charged with magnetic stir bar. Then the reaction tube was evacuated and back filled with nitrogen. This vacuum/ nitrogen sequence was repeated for four times. DMSO (5 mL) was added under the positive pressure of nitrogen and the resealed tube was immersed in a preheated oil bath at 90 ºC and stirred vigorously for 24 hours. The reaction mixture was cooled to room temperature, diluted with 5 mL ethyl acetate and extracted with brine solution 3 times. Total organic part was dried over anhyd. Na_2SO_4 and purified by column chromatography.



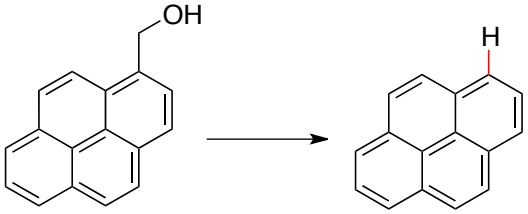
Naphthalene (entry 1). Reaction was done by general procedure A running for 36 h with naphthalen-2-ylmethanol (0.5 mmol, 79 mg) and 16 mol% palladium acetate (0.08 mmol, 18 mg) loading and ethylcyclohexane as solvent. Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 60–120). White crystalline naphthalene was eluted by pet ether only. Isolated yield 88% (56 mg). Mp: 79-80 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.46 – 7.53 (dd, *J* = 6.3, 3.2 Hz, 4H), 7.82 – 7.90 (dd, *J* = 6.2, 3.3 Hz, 4H). ^{13}C NMR (101 MHz, Chloroform-d) δ 126.02, 128.08, 133.62. GC–MS (*m/z*): 128.1 $[M]^+$. Isolated side product 2-methyl naphthalene 7% (5 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 2.53 – 2.57 (d, *J* = 1.1 Hz, 3H), 7.32 – 7.38 (dt, *J* = 8.4, 1.5, 1.5 Hz, 1H), 7.41 – 7.52 (m, 2H), 7.63 – 7.67 (s, 1H), 7.76 – 7.86 (m, 3H). ^{13}C NMR (101 MHz, $cdcl_3$) δ 21.92, 125.14, 126.05, 127.02, 127.42, 127.79, 127.87, 128.31, 131.87, 133.84, 135.63. GC–MS (*m/z*): 142.1 $[M]^+$.



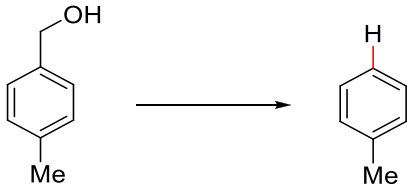
Naphthalene (entry 2). Reaction was done by general procedure A running for 48 h with naphthalen-1-ylmethanol (0.5 mmol, 79 mg) and 16 mol% palladium acetate (0.08 mmol, 18 mg) loading and ethylcyclohexane as solvent. Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 60–120). White crystalline naphthalene was eluted by pet ether only. Isolated yield 70% (44 mg). Mp: 79-80 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.32 – 7.67 (m, 2H), 7.67 – 8.11 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 126.02, 128.08, 133.64. GC–MS (*m*/*z*): 128.2 $[M]^+$. Isolated side product 1-methyl naphthalene 12% (8 mg). GC–MS (*m*/*z*): 142.1 $[M]^+$.



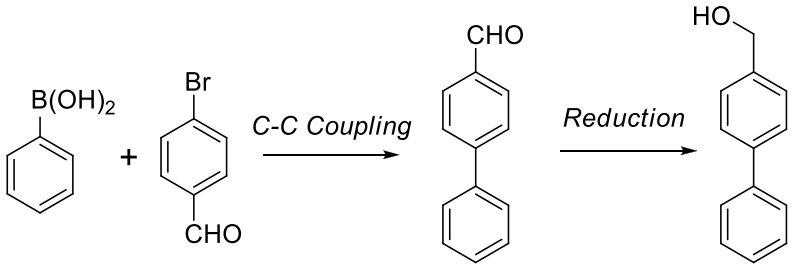
Anthracene (entry 3). Reaction was done by general procedure A for 24 h with anthracen-9-ylmethanol (0.5 mmol, 105 mg) and 12 mol% palladium acetate (0.06 mmol, 14 mg) loadingand cyclohexane as solvent. Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 60–120). White crystalline anthracene was eluted by pet ether only. Isolated yield 74% (65 mg). Mp: >180 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.38 – 7.57 (m, 4H), 7.93 – 8.08 (m, 4H), 8.38 – 8.53 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ125.54, 126.42, 128.36, 131.87. GC–MS (*m*/*z*): 178.2 $[M]^+$. Side product detected 9-methylanthracene, yield 15%, GC–MS (*m*/*z*): 192.1 $[M]^+$.



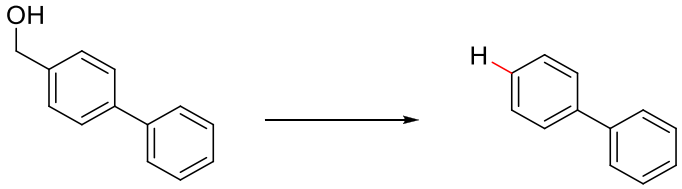
Pyrene (entry 4). Reaction was done by general procedure A for 36 h with pyren-1-ylmethanol (0.5 mmol, 116 mg) and 16 mol% palladium acetate (0.08 mmol, 18 mg) loading and ethylcyclohexane as solvent. Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 60–120). White crystalline pyrene was eluted by pet ether only. Isolated yield 88% (88 mg). Mp: 146-147 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.01 – 8.07 (dd, J = 8.1, 7.2 Hz, 2H), 8.09 – 8.13 (s, 4H), 8.19 – 8.24 (d, J = 7.6 Hz, 4H). ^{13}C NMR (101 MHz, Chloroform-d) δ 125.16, 125.98, 127.60, 131.35. GC–MS (*m*/*z*): 202.1 $[M]^+$. Side product detected 1-methylpyrene, yield 5%, GC–MS (*m*/*z*): 216.1 $[M]^+$.



Toluene (entry 5). Reaction was done by general procedure A for 48 h with p-tolylmethanol (0.5 mmol, 61 mg) and 16 mol% palladium acetate (0.08 mmol, 18 mg) loading and cyclohexane as solvent. Yield was determined by gas chromatography using n-decane as internal standard. GC yield 85%. GC–MS (*m/z*): 91.1 $[M]^+$. Side product 1,4-dimethylbenzene, GC yield 9%, GC–MS (*m/z*): 106.1 $[M]^+$. Using ethylcyclohexane as solvent and running reaction for 36 h, GC yield 57%. GC–MS (*m/z*): 91.1 $[M]^+$. Side product detected 1,4-dimethylbenzene, GC yield 19%, GC–MS (*m/z*): 106.1 $[M]^+$ and otherwise starting material remained unreacted. With 8 mol% catalyst loading in cyclohexane solvent, running reaction upto 24 h GC yield of the desired product 52%. Side porduct detecteted 1,4-dimethylbenzene, GC yield 5%.

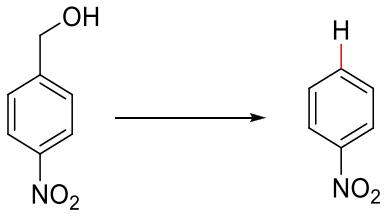


Biphenyl-4-ylmethanol. C-C coupling was done following general procedure D with phenylboronic acid (1.1 mmol, 134 mg). Reaction mixture was reduced following general procedure B. White crystalline biphenyl-4-ylmethanol was isolated through silica gel (60-120 mesh), eluted by pet ether –ethyl acetate mixture (90:10 v/v). Mp: 94-95 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 4.72 – 4.77 (s, 2H), 7.31 – 7.40 (m, 1H), 7.40 – 7.49 (m, 4H), 7.56 – 7.64 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-d) δ 65.33, 127.30, 127.54, 127.68, 128.99, 140.06, 140.86, 141.02.

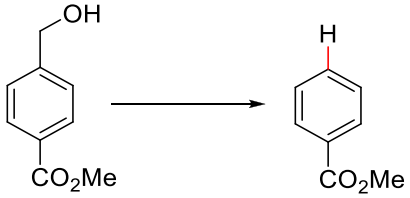


Biphenyl (entry 6). Reaction was done by general procedure A for 48 h with biphenyl-4-ylmethanol(0.25 mmol, 46 mg), Na_2CO_3 (0.375 mmol, 39 mg), 16 mol% palladium acetate (0.04 mmol, 9 mg) loading and cyclohexane (1 mL) as solvent. Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 100–200). White crystalline biphenyl was eluted by pet ether only. Isolated yield 93% (36 mg). Mp: 69-70 °C.^{1}H NMR (400 MHz, Chloroform-d) δ 7.30 – 7.40 (m, 2H), 7.41 – 7.53 (m, 4H), 7.53 – 7.74 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-d) δ 127.37, 128.96, 141.43. GC–MS (*m/z*): 154.1 $[M]^+$. Using ethylcyclohexane as solvent and running reaction for 36 h isolated yield 71% (27 mg). Side product isolated 4-methylbiphenyl 12% (5 mg). ^{1}H NMR (400

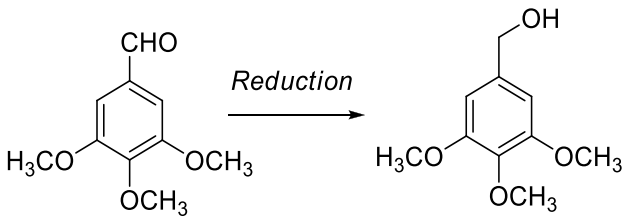
MHz, Chloroform-d) δ 2.40 – 2.42 (s, 3H), 7.22 – 7.32 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.38 (m, 1H), 7.41 – 7.48 (m, 2H), 7.49 – 7.54 (dd, *J* = 9.0, 2.6 Hz, 2H), 7.57 – 7.62 (m, 2H). ^{13}C NMR (101 MHz, cdcl$_3$) δ 21.32, 127.17, 127.19, 128.91, 129.67, 133.33, 137.22, 138.56.



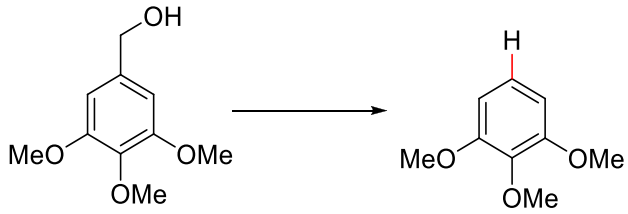
Nitrobenzene (entry 7). Reaction was done by general procedure A for 24 h with (4-nitrophenyl)methanol (0.5 mmol, 77 mg) and 12 mol% palladium acetate (0.06 mmol, 14 mg) loadingand cyclohexane (1.3 mL) as solvent. Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Yellow liquid nitrobenzene was eluted by pet ether only. Isolated yield 73% (44 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.51 – 7.63 (m, 2H), 7.67 – 7.77 (m, 1H), 8.20 – 8.33 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 123.71, 129.51, 134.78, 148.45. GC–MS (*m*/*z*): 123.1 [M]$^+$. Side product aniline, GC yield 9%, GC–MS (*m*/*z*): 93.1 [M]$^+$. Using ethylcyclohexane as solvent and running reaction for 48 h isolated yield 60% (37 mg). Side product aniline, GC yield 14%, GC–MS (*m*/*z*): 93.1 [M]$^+$. With 8 mol% catalyst loading, cyclohexane as solvent and for reaction time 24 h, isolated yield of nitro benzene 61%. Side product aniline, GC yield 7%. GC–MS (*m*/*z*): 93.1 [M]$^+$.



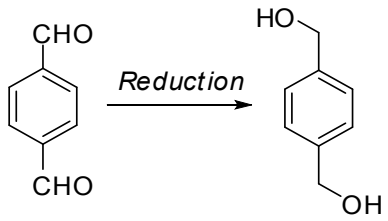
Methyl benzoate (entry 8). Reaction was done by general procedure A for 36 h with methyl 4-(hydroxymethyl)benzoate (0.5 mmol, 83 g) and 12 mol% palladium acetate (0.06 mmol, 14 mg) loading and cyclohexane (1.3 mL) as solvent. Isolated yield 83% (56 mg). Colourless liquid methyl benzoate was isolated through silica gel (60-120 mesh), eluted by pet ether –ethyl acetate mixture (99:1 v/v). ^{1}H NMR (400 MHz, Chloroform-d) δ 3.83 – 4.02 (s, 3H), 7.37 – 7.48 (m, 2H), 7.48 – 7.64 (m, 1H), 7.96 – 8.12 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 52.23, 128.49, 129.71, 130.29, 133.05, 167.25. GC–MS (*m*/*z*): 136.0 [M]$^+$. Side product, methyl 4-methylbenzoate GC yield 6%, GC–MS (*m*/*z*): 150.1. Using ethylcyclohexane as solvent and running reaction for 36 h, Isolated yield 68%. Side product detected, GC yield 10%, GC–MS (*m*/*z*): 150.1. Otherwise starting material remained unreacted. In 10 mol% catalyst loading, cyclohexane as solvent and running reaction for 24 h, GC yield of the product was 72%. Side product methyl 4-methylbenzoate, GC yield 9%, GC–MS (*m*/*z*): 150.1. Otherwise starting material remained unreacted.



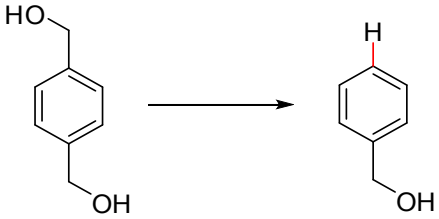
(3,4,5-Trimethoxyphenyl)methanol. Aldehyde was reduced following general procedure B. Pale yellowish liquid biphenyl-4-ylmethanol was isolated through silica gel (60-120 mesh), eluted by pet ether –ethyl acetate mixture (90:10 v/v). ^{1}H NMR (400 MHz, Chloroform-d) δ 3.81 – 3.83 (s, 3H), 3.83 – 3.86 (s, 6H), 4.58 – 4.65 (m, 2H), 6.54 – 6.62 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 56.22, 61.02, 65.58, 103.89, 136.87, 137.30, 153.45. GC–MS (*m/z*): 198.1 $[M]^+$.



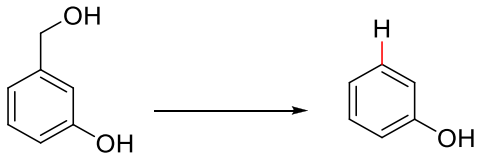
1,2,3–trimethoxybenzene (entry 9). Reaction was done by general procedure A for 48 h with (3,4,5-trimethoxyphenyl)methanol (0.5 mmol, 99 mg) and 16 mol% palladium acetate (0.08 mmol, 18 mg) loadingand cyclohexane (1.3 mL) as solvent. Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Colorless dense liquid product was eluted by pet ether –ethyl acetate mixture (95:5 v/v). Isolated yield 86% (73 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 3.62 – 4.11 (d, *J* = 2.1 Hz, 9H), 6.46 – 6.66 (d, *J* = 8.4 Hz, 2H), 6.91 – 7.06 (t, *J* = 8.4, 8.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 56.13, 60.91, 105.24, 123.77, 138.12, 153.59. GC–MS (*m/z*): 168.1 $[M]^+$. Otherwise starting material remained unreacted.



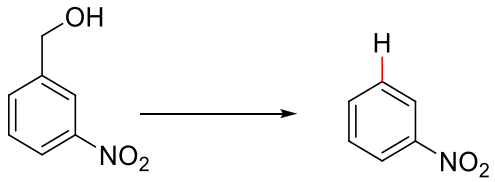
1,4-Phenylenedimethanol. Aldehyde was reduced following general procedure B. White crystalline solid 1,4-Phenylenedimethanol was isolated through silica gel (60-120 mesh), eluted by pet ether –ethyl acetate mixture (85:15 v/v). Mp: 117-118 °C.^{1}H NMR (400 MHz, DMSO-d6) δ 4.45 – 4.46 (d, *J* =5.7 Hz, 4H), 5.18 – 5.21 (t, *J* =5.7, 5.7 Hz, 2H), 7.24 (s, 4H).



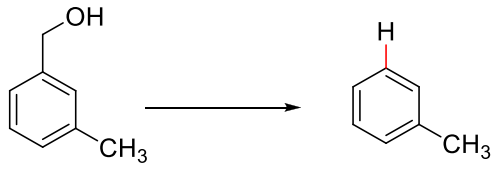
Benzylalcohol (entry 10). Reaction was done by general procedure A for 36 h with 1,4-Phenylenedimethanol(0.5 mmol, 92 mg) and 16 mol% palladium acetate (0.08 mmol, 18 mg) loading and cyclohexane (1.3 mL) as solvent. Isolated yield 60%. ^{1}H NMR (400 MHz, Chloroform-d) δ 2.27 – 2.75 (b, 1H), 4.48 – 4.75 (d, *J* = 3.9 Hz, 2H), 7.22 – 7.47 (m, 5H).^{13}C NMR (101 MHz, Chloroform-d) δ 65.29, 127.15, 127.73, 128.66, 140.96.GC–MS (*m/z*): 108.2 $[M]^+$. GC yield of benzaldehyde 4%. GC–MS (*m/z*): 106.1 $[M]^+$. GC yield of benzene 8%.



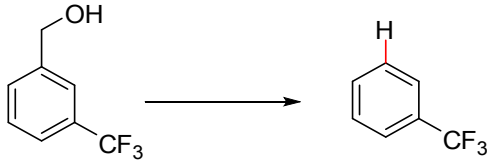
Phenol (entry 11). Reaction was done by general procedure A for 24 h with 3-(hydroxymethyl)phenol (0.5 mmol, 62 mg) and 12 mol% palladium acetate (0.06 mmol, 14mg) loading and cyclohexane (1.3 mL) as solvent. Colorless dense liquid product was eluted by pet ether –ethyl acetate mixture (97:3 v/v). Isolated yield 45% (21 mg). GC–MS (*m/z*): 94.0 $[M]^+$. ^{1}H NMR (400 MHz, Chloroform-d) δ 4.81 – 5.29 (s, 1H), 6.78 – 6.88 (m, 2H), 6.89 – 7.00 (m, 1H), 7.09 – 7.49 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 115.51, 120.95, 129.87, 155.70. Side product, detected 3-methyl phenol, isolated yield 20%, GC–MS (*m/z*): 108.1 $[M]^+$. ^{1}H NMR (400 MHz, Chloroform-d) δ 2.84 (s, 3H), 5.81 (s, 1H), 6.62 – 6.74 (m, 2H), 7.08 – 7.12 (m, 1H), ^{13}C NMR (101 MHz, cdcl$_3$) δ 21.37, 112.35, 116.11, 121.60, 129.46, 139.87, 155.41. Otherwise rest of the starting material remained unreacted.



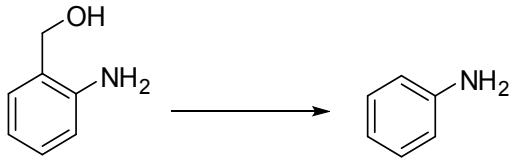
Nitrobenzene (entry 12). Reaction was done by general procedure A for 24 h with (3-nitrophenyl)methanol (0.5 mmol, 77 mg) and 12 mol% palladium acetate (0.08 mmol, 18 mg) loading and cyclohexane (1.3 mL) as solvent. Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Yellow liquid nitrobenzene was eluted by pet ether only. Isolated yield 73% (44 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.49 – 7.62 (m, 2H), 7.64 – 7.81 (m, 1H), 8.13 – 8.34 (m, 2H). ^{13}C NMR (101 MHz, cdcl$_3$) δ 123.67, 129.47, 134.74. GC–MS (*m/z*): 123.1 $[M]^+$. Side product aniline, GC yield 5 %, GC–MS (*m/z*): 93.1 $[M]^+$. Using ethylcyclohexane as solvent and running reaction for 48 h isolated yield 58%. Side product detected aniline, Isolated yield 12 %. ^{1}HNMR and ^{13}CNMR data are exactly matched with our data (entry 15). GC–MS (*m/z*): 93.1 $[M]^+$. Otherwise rest of the starting material remained unreacted.



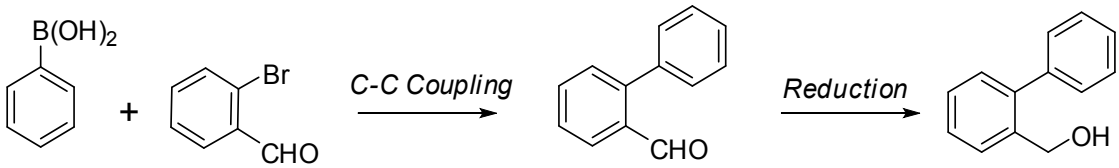
Toluene (entry 13). Reaction was done by general procedure A for 48 h with methyl m-tolylmethanol (0.5 mmol, 61 mg) and 8 mol% palladium acetate (0.04 mmol, 9 mg) loadingand cyclohexane (1.3 mL) as solvent. Yield was determined by gas chromatography using n-decane as internal standard. GC yield 54%. GC–MS (*m/z*): 91.1 $[M]^+$. Side product 1,3-dimethylbenzene, GC yield 9%, GC–MS (*m/z*): 106.1 $[M]^+$. Otherwise rest of the starting material remained unreacted.



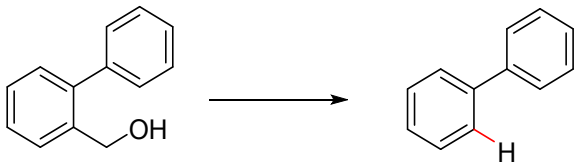
(Trifluoromethyl)benzene (entry 14). Reaction was done by general procedure A for 48 h with methyl (3-(trifluoromethyl)phenyl)methanol (0.5 mmol, 88 mg) and 16 mol% palladium acetate (0.08 mmol, 18 mg) loadingand cyclohexane (1.3 mL) as solvent. Yield was determined by gas chromatography using n-decane as internal standard. GC yield 64%. GC–MS (*m/z*): 146.0 $[M]^+$. Otherwise rest of the starting material remained unreacted.



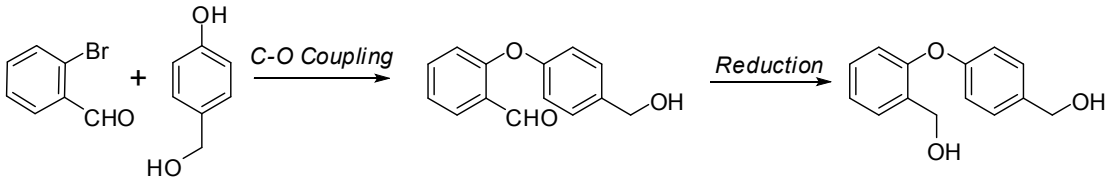
Aniline (entry 15). Reaction was done by general procedure A for 48 h with (2-aminophenyl)methanol (0.5 mmol, 62 mg) and 16 mol% palladium acetate (0.08 mmol, 18 mg) loadingand cyclohexane (1.3 mL) as solvent. Brown liquid product was eluted by pet ether –ethyl acetate mixture (95:5 v/v). Isolated yield 42%. ^{1}H NMR (400 MHz, Chloroform-d) δ 3.16 – 4.08 (s, 2H), 6.66 – 6.73 (m, 2H), 6.73 – 6.83 (tt, *J* = 7.4, 7.4, 1.1, 1.1 Hz, 1H), 7.11 – 7.23 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 115.30, 118.76, 129.48, 146.53. GC–MS (*m/z*):93.1 $[M]^+$. Side product detected 2-methyl aniline, GC yield 15%, GC–MS (*m/z*): 107.1 $[M]^+$; 2-amino benzaldehyde, yield 5%, GC–MS (*m/z*): 121.1 $[M]^+$. Otherwise rest of the starting material remained unreacted.



Biphenyl-2-ylmethanol. C-C coupling was done following general procedure D with phenylboronic acid (1.1 mmol, 134 mg). Reaction mixture was reduced following general procedure B. White crystalline biphenyl-4-ylmethanol was isolated through silica gel (60-120 mesh), eluted by pet ether –ethyl acetate mixture (90:10 v/v). ^{1}H NMR (400 MHz, Chloroform-d) δ 4.55 – 4.78 (s, 2H), 7.27 – 7.32 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.33 – 7.47 (m, 7H), 7.52 – 7.60 (dd, *J* = 7.2, 1.7 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 63.38, 127.46, 127.88, 127.92, 128.46, 128.60, 129.32, 130.28, 138.20, 140.82, 141.50.

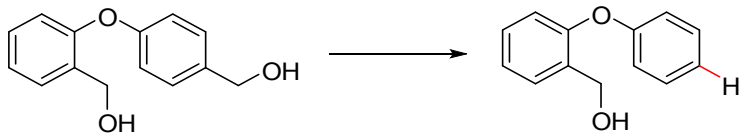


Biphenyl (entry 16). Reaction was done by general procedure A for 48 h with biphenyl-2-ylmethanol (0.25 mmol, 46 mg), Na_2CO_3 (0.375 mmol, 39 mg), 16 mol% palladium acetate (0.04 mmol, 9 mg) loading and cyclohexane (1 mL) as solvent. Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 100–200). White crystalline biphenyl was eluted by pet ether only. Isolated yield 59% (23 mg).Mp: 69-70 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.31 – 7.39 (m, 2H), 7.40 – 7.51 (m, 4H), 7.54 – 7.68 (m, 4H).^{13}C NMR (101 MHz, $CDCl_3$) δ 127.37, 128.96, 141.43. GC–MS (*m/z*): 154.1 $[M]^+$. Otherwise rest of the starting material remained unreacted.

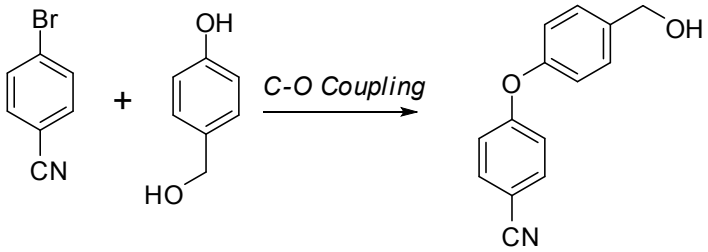


(2-(4-(Hydroxymethyl)phenoxy)phenyl)methanol. C-O coupling was done by general procedure E with 4-(hydroxymethyl)phenol (2.5 mmol, 310 mg) and 4-bromobenzaldehyde (3 mmol, 555 mg). Desired product was purified by column chromatography (60–120 mesh), Colorless liquidaldehyde was eluted by pet ether – ethyl acetate mixture (95:5 v/v). ^{1}H NMR (400 MHz, Chloroform-d) δ 4.62 – 4.79 (s, 2H), 6.83 – 6.93 (dq, *J* = 8.5, 1.0, 1.0, 0.8 Hz, 1H), 7.01 – 7.10 (dd, *J* = 8.4, 1.5 Hz, 2H), 7.13 – 7.22 (m, 1H), 7.35 – 7.44 (m, 2H), 7.44 – 7.57 (dddt, *J* = 8.0, 7.3, 1.8, 0.8, 0.8 Hz, 1H), 7.87 – 7.97 (m, 1H), 10.42 – 10.54 (m, 1H). Aldehyde was reduced following general procedure B. Colorless liquid (2-(4-(hydroxymethyl)phenoxy)phenyl)methanol was isolated through silica gel (60-120 mesh), eluted by pet ether –ethyl acetate mixture (90:10 v/v). ^{1}H NMR (400 MHz, Chloroform-d) δ 4.62 – 4.70 (s, 2H), 4.69 – 4.79 (s, 2H), 6.82 – 6.92 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.91 – 7.03 (m, 2H), 7.08 – 7.20 (td, *J* = 7.5, 7.4, 1.2 Hz, 1H), 7.20 – 7.30 (m, 1H), 7.29 – 7.40 (m, 2H), 7.40 – 7.55 (dd, *J* = 7.6, 1.8 Hz, 1H). ^{13}C NMR (101

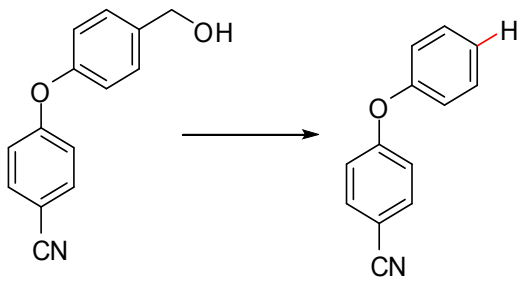
MHz, Chloroform-d) δ 61.26, 64.93, 118.57, 118.81, 124.08, 128.96, 129.23, 129.44, 132.05, 136.03, 154.78, 156.84.



(2-Phenoxyphenyl)methanol (entry 17). Reaction was done by general procedure A for 48 h with (2-(4-(hydroxymethyl)phenoxy)phenyl)methanol (0.15 mmol, 35 mg), Na_2CO_3(0.225 mmol, 24 mg), 12 mol% palladium acetate (0.018 mmol, 4 mg) loading and cyclohexane (1 mL) as solvent. Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 100–200). White crystalline 4-phenoxybenzonitrile was eluted by pet ether –ethyl acetate mixture (90:10 v/v). Isolated yield 47% (14 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 4.73 – 4.77 (m, 2H), 6.81 – 6.93 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.94 – 7.04 (m, 2H), 7.05 – 7.18 (dddd, *J* = 10.8, 8.5, 7.3, 1.2 Hz, 2H), 7.21 – 7.30 (td, *J* = 7.9, 7.7, 1.8 Hz, 1H), 7.29 – 7.40 (m, 2H), 7.40 – 7.51 (dd, *J* = 7.5, 1.7 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 61.48, 118.60, 118.81, 123.56, 123.99, 129.24, 129.46, 130.06, 132.08, 154.94, 157.30. Side product detected diphenylether, GC yield 8%. Otherwise almost rest of the starting material remained unreacted.

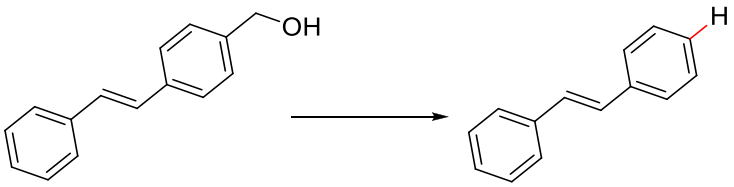


4-(4-(Hydroxymethyl)phenoxy)benzonitrile. C-O coupling was done by general procedure Ewith 4-bromobenzonitrile (2.5 mmol, 320 mg), 4-(hydroxymethyl)phenol (3 mmol, 372 mg). Desired product was purified by column chromatography (60–120 mesh). White solid 4-(4-(hydroxymethyl)phenoxy)benzonitrile was eluted by pet ether –ethyl acetate mixture (90:10 v/v). Mp: 79-80 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 1.77 (t, 1H), 4.72 – 4.73 (s, 2H), 6.99 – 7.02 (m, 2H), 7.02 – 7.08 (m, 2H), 7.41 – 7.43 (m, 2H), 7.59 – 7.61 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 64.88, 106.07, 118.09, 119.03, 120.71, 129.16, 134.36, 137.95, 154.45, 161.84.

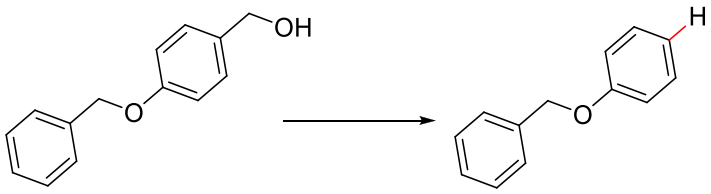


4-Phenoxybenzonitrile(entry 18). Reaction was done by general procedure A for 48 h with 4-(4-(hydroxymethyl)phenoxy)benzonitrile (0.25 mmol, 56 mg), Na_2CO_3

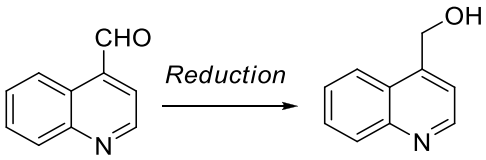
(0.375 mmol, 39 mg), 16 mol% palladium acetate (0.04 mmol, 9 mg) loading and cyclohexane (1 mL) as solvent. Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 100–200). White crystalline 4-phenoxybenzonitrile was eluted by pet ether only. Isolated yield 86% (42 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.98 – 7.03 (dq, *J* = 9.5, 2.4, 2.4, 2.2 Hz, 2H), 7.04 – 7.09 (m, 2H), 7.16 – 7.33 (m, 1H), 7.36 – 7.48 (m, 2H), 7.53 – 7.66 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 105.96, 118.09, 119.07, 120.61, 125.35, 130.43, 134.33, 154.97, 161.86. GC–MS (*m/z*): 195.1 $[M]^+$. Otherwise almost rest of the starting material remained unreacted.



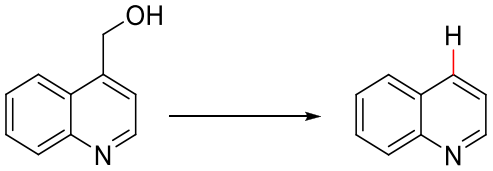
(E)–1,2–Diphenylethene (entry 19). Reaction was done by general procedure A for 36 h with (E)-(4-styrylphenyl)methanol (0.25 mmol, 53 mg) and 16 mol% palladium acetate (0.04 mmol, 9 mg) loading and ethylcyclohexane as solvent (1 mL). Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 60–120). White crystalline product was eluted by pet ether only. Isolated yield 72% (32 mg).Mp: 122 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.09 – 7.15 (s, 2H), 7.20 – 7.30 (m, 2H), 7.30 – 7.44 (t, *J* = 7.6, 7.6 Hz, 4H), 7.46 – 7.58 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 126.71, 127.83, 128.89, 137.52. GC–MS (*m/z*): 180.2 $[M]^+$. Side product detected 1,2-diphenylethane, GC yield 20%, GC–MS (*m/z*): 182.1 $[M]^+$.



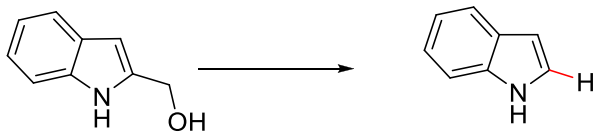
Benzyloxybenzene(entry 20). Reaction was done by general procedure A for 48 h with (E)-(4-styrylphenyl)methanol (0.25 mmol, 54 mg), Na_2CO_3 (0.375 mmol, 39 mg) and 16 mol% palladium acetate (0.04 mmol, 9 mg) loading and ethylcyclohexane as solvent (1 mL). Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Colorless dense liquid product was eluted by pet ether only. Isolated yield 56% (26 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 5.08 – 5.10 (s, 2H), 6.93 – 7.04 (m, 3H), 7.28 – 7.53 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 70.08, 115.02, 121.13, 127.69, 128.14, 128.78, 129.68, 137.24, 158.96. GC–MS (*m/z*): 184.1 $[M]^+$. Side product phenol, isolated yield 20%, GC–MS (*m/z*): 94.1 $[M]^+$; 1-(benzyloxy)-4-methylbenzene GC yield 5%, GC–MS (*m/z*): 108.1 $[M]^+$. Otherwise almost rest of the starting material remained unreacted.



Quinolin-4-ylmethanol. Aldehyde was reduced following general procedure B. Brown solid quinolin-4-ylmethanol was isolated through silica gel (60-120 mesh), eluted by pet ether –ethyl acetate mixture (80:20 v/v). Mp: 143-147 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 5.20 – 5.27 (d, *J* = 1.1 Hz, 2H), 7.52 – 7.62 (m, 2H), 7.69 – 7.77 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.92 – 8.00 (ddd, *J* = 8.4, 1.5, 0.7 Hz, 1H), 8.11 – 8.19 (dt, *J* = 8.4, 0.9, 0.9 Hz, 1H), 8.84 – 8.92 (d, *J* = 4.4 Hz, 1H).

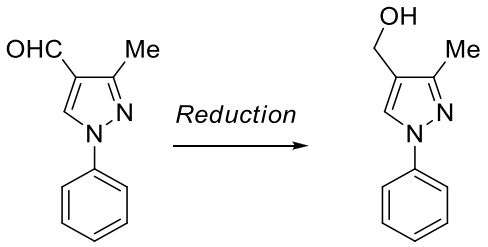


Quinoline (entry 21). Reaction was done by general procedure A for 48 h with quinolin-4-ylmethanol (0.5 mmol, 79 mg) and 16 mol% palladium acetate (0.08 mmol, 18 mg) loading and cyclohexane as solvent (1.3 mL). Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Yellow liquid quinoline was eluted by pet ether – ethyl acetate mixture (90:10 v/v). Isolated yield 91% (59 mg).^{1}H NMR (400 MHz, Chloroform-d) δ 7.31 – 7.41 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.46 – 7.56 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.64 – 7.74 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.73 – 7.84 (dd, *J* = 8.2, 1.5 Hz, 1H), 8.05 – 8.23 (dd, *J* = 8.3, 1.4 Hz, 2H), 8.81 – 9.03 (dd, *J* = 4.3, 1.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 121.18, 126.71, 127.89, 128.37, 129.21, 129.67, 136.40, 148.03, 150.28. GC–MS (*m/z*): 129.1 $[M]^+$. Otherwise almost rest of the starting material remained unreacted.

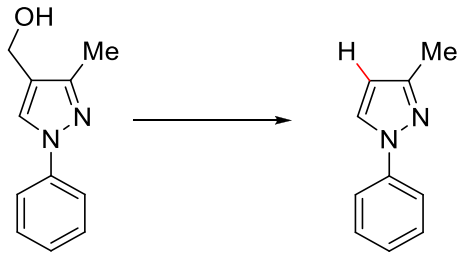


1H–Indole (entry 22). Reaction was done by general procedure A for 24 h with 1H–indole–3–carbaldehyde (0.25 mmol, 36 mg), ethylcyclohexane (1 mL), Na_2CO_3(0.375 mmol, 39 mg) and 16 mol% palladium acetate (0.04 mmol, 9 mg) loading. Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 60–120). White crystalline solid 1H–indolewas eluted by pet ether –ethyl acetate mixture (98:2 v/v). Isolated yield 52% (15 mg). Mp: 52-53 °C.^{1}H NMR (400 MHz, Chloroform-d) δ 6.46 – 6.67 (ddt, *J* = 3.1, 2.1, 1.0, 1.0 Hz, 1H), 7.09 – 7.16 (m, 2H), 7.16 – 7.24 (ddd, *J* = 8.1, 6.3, 1.2 Hz, 1H), 7.28 – 7.39 (ddd, *J* = 8.1, 2.6, 1.2 Hz, 1H), 7.60 – 7.70 (d, *J* = 7.8 Hz, 1H), 7.86 – 8.08 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 102.77, 111.21, 119.98, 120.91, 122.15,

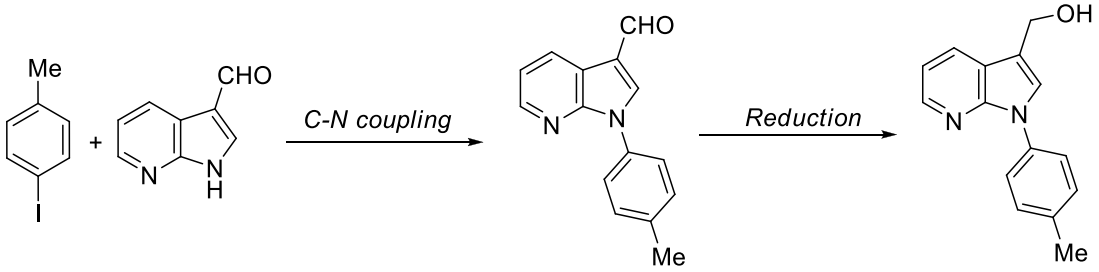
124.32, 128.00, 135.93. GC–MS (*m/z*): 117.1 $[M]^+$. Otherwise almost rest of the starting material remained unreacted.



(3-Methyl-1-phenyl-1H-pyrazol-4-yl)methanol. Aldehyde was reduced following general procedure B. Brown solid (3-Methyl-1-phenyl-1H-pyrazol-4-yl)methanol was isolated through silica gel (60-120 mesh), eluted by pet ether –ethyl acetate mixture (90:10 v/v).

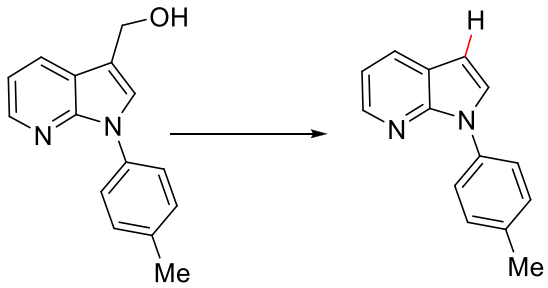


3–Methyl–1–phenyl–1H–pyrazole (entry 23). Reaction was done by general procedure A for 48 h with (3-Methyl-1-phenyl-1H-pyrazol-4-yl)methanol (0.5 mmol, 94 mg), cyclohexane (1.3 mL), Na_2CO_3 (0.375 mmol, 39 mg) and 16 mol% palladium acetate (0.08 mmol, 18 mg) loading. Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Colorless liquid 3–Methyl–1–phenyl–1H–pyrazolewas eluted by pet ether –ethyl acetate mixture (99:1 v/v). Isolated yield 66% (49 mg).^{1}H NMR (400 MHz, Chloroform-d) δ 2.31 – 2.50 (s, 3H), 6.16 – 6.34 (d, *J* = 2.4 Hz, 1H), 7.18 – 7.29 (m, 1H), 7.36 – 7.50 (m, 2H), 7.59 – 7.70 (m, 2H), 7.77 – 7.88 (d, *J* = 2.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 13.93, 107.69, 118.97, 126.09, 127.53, 129.52, 140.35, 150.70. GC–MS (*m/z*): 158.1 $[M]^+$. Otherwise almost rest of the starting material remained unreacted.

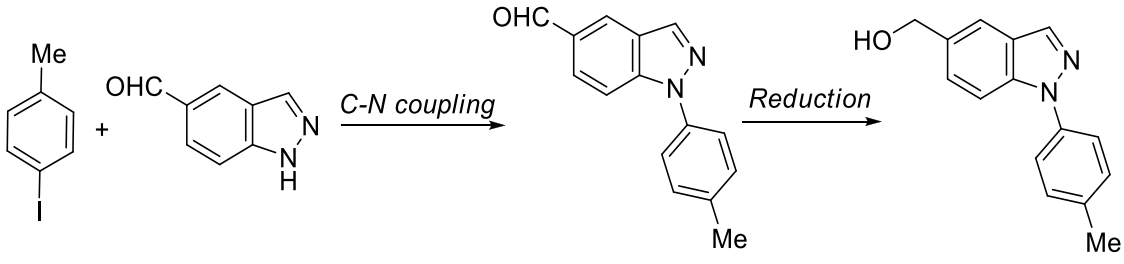


(1-p-tolyl-1H-pyrrolo[2,3-b]pyridin-3-yl)methanol. Following general procedure C, *p*–tolyl iodide (1.5 mmol, 327 mg); 1H-pyrrolo[2,3-b]pyridine-3-carbaldehyde (1.5

mmol, 219 mg); CuI (0.3 mmol, 28 mg); 1,10–phenanthrolene (0.6 mmol, 59 mg) and K_2CO_3 (3 mmol, 414 mg) were used. Column chromatography provided the desired compound as white solid using pet ether –ethyl acetate mixture (90:10 v/v) as eluent.Aldehyde was reduced following general procedure B. Colorlessliquid(1-p-tolyl-1H-pyrrolo[2,3-b]pyridin-3-yl)metanol was isolated through silica gel (60-120 mesh), eluted by pet ether –ethyl acetate mixture (80:20 v/v). ^{1}H NMR (400 MHz, Chloroform-d) δ 2.35 – 2.48 (s, 3H), 4.85 – 4.96 (d, *J* = 0.8 Hz, 2H), 7.08 – 7.17 (dd, *J* = 7.9, 4.7 Hz, 1H), 7.28 – 7.37 (m, 2H), 7.42 – 7.49 (d, *J* = 0.8 Hz, 1H), 7.51 – 7.61 (m, 2H), 8.01 – 8.10 (dd, *J* = 7.8, 1.6 Hz, 1H), 8.31 – 8.45 (dd, *J* = 4.7, 1.6 Hz, 1H).

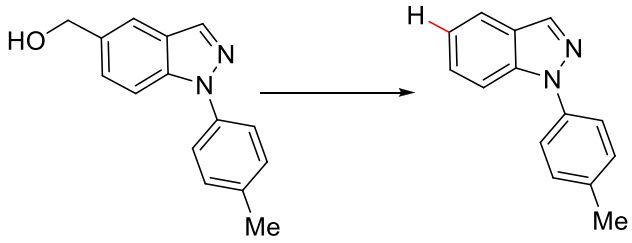


1–*p*–Tolyl–1H–pyrrolo[2,3–b]pyridinepyrazole (entry 24). Reaction was done by general procedure A for 48 h with 1–p–tolyl–1H–pyrrolo[2,3–b]pyridine–5–carbaldehyde (0.25 mmol, 59 mg), cyclohexane (1 mL), Na_2CO_3 (0.375 mmol, 39 mg) and 16 mol% palladium acetate (0.04 mmol, 9 mg) loading. Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Yellow oily liquid (1-p-tolyl-1H-pyrrolo[2,3-b]pyridin-3-yl)methanolwas eluted by pet ether –ethyl acetate mixture (99:1 v/v). Isolated yield 90% (46 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 2.34 – 2.50 (s, 3H), 6.54 – 6.78 (dd, *J* = 3.6, 1.3 Hz, 1H), 7.03 – 7.18 (ddd, *J* = 7.5, 4.7, 1.3 Hz, 1H), 7.28 – 7.39 (d, *J* = 8.0 Hz, 2H), 7.45 – 7.51 (m, 1H), 7.58 – 7.65 (m, 2H), 7.93 – 8.00 (d, *J* = 7.8 Hz, 1H), 8.34 – 8.40 (d, *J* = 4.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.23, 101.40, 116.68, 123.84, 124.25, 128.20, 130.02, 130.08, 136.12, 136.38, 143.55, 147.71. GC–MS (*m/z*): 208.0 $[M]^+$.

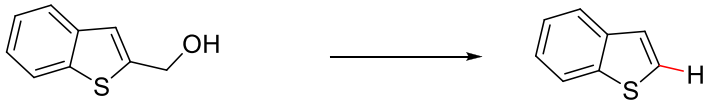


(1-p-tolyl-1H-indazol-5-yl)methanol. Following general procedure C, *p*–tolyl iodide (1.5 mmol, 327 mg); 1*H*–indazole–5–carbaldehyde (1.5 mmol, 219 mg); CuI (0.3 mmol, 28 mg); 1,10–phenanthrolene (0.6 mmol, 59 mg) and K_3PO_4 (3 mmol, 637 mg) were used. Column chromatography provided the desired product as white crystalline solid using pet ether –ethyl acetate mixture (95:5 v/v) as eluent. Aldehyde was

reduced following general procedure B. Brown crystaline solid (1-p-tolyl-1H-indazol-5-yl)methanol was isolated through silica gel (60-120 mesh), eluted by pet ether – ethyl acetate mixture (90:10 v/v). Mp: 69-70 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 2.40 – 2.48 (s, 3H), 4.73 – 4.84 (s, 2H), 7.28 – 7.37 (m, 2H), 7.39 – 7.48 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.54 – 7.62 (m, 2H), 7.64 – 7.71 (dt, *J* = 8.7, 0.9, 0.9 Hz, 1H), 7.71 – 7.77 (dq, *J* = 1.6, 0.8, 0.8, 0.8 Hz, 1H), 8.06 – 8.19 (d, *J* = 1.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 21.29, 65.54, 110.85, 119.63, 122.85, 127.14, 130.20, 134.42, 135.16, 135.23, 136.84, 137.75, 138.61.

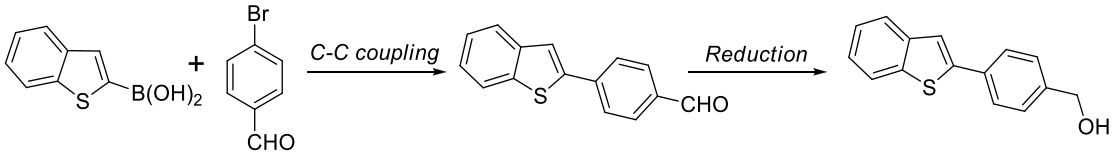


1-p-tolyl-1H-indazole (entry 25). Reaction was done by general procedure A for 48 h with 1–p–tolyl–1H–indazole–5–carbaldehyde (0.25 mmol, 59 mg), Na_2CO_3 (0.375 mmol, 39 mg), cyclohexane (1 mL) and 16 mol% palladium acetate (0.04 mmol, 9 mg) loading. Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Yellow liquid 1–p–Tolyl–1H–indazolewas eluted by pet ether –ethyl acetate mixture (98.5:1.5 v/v). Isolated yield 74% (38 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 2.38 – 2.45 (m, 3H), 7.14 – 7.26 (m, 1H), 7.26 – 7.52 (m, 3H), 7.52 – 7.64 (dt, *J* = 10.7, 3.8, 3.8 Hz, 2H), 7.64 – 7.89 (ddt, *J* = 33.4, 9.1, 4.4, 4.4 Hz, 2H), 8.12 – 8.31 (q, *J* = 4.7, 4.7, 4.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 21.29, 110.59, 121.45, 121.54, 122.95, 125.32, 127.18, 130.18, 135.22, 136.74, 137.90, 138.97.GC–MS (*m/z*): 208.1 $[M]^+$. Side product 1-p-tolyl-1H-indazole-5-carbaldehyde, isolated yield 5% (4 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 1.51 – 1.76 (s, 1H), 2.36 – 2.63 (s, 3H), 7.30 – 7.50 (m, 2H), 7.50 – 7.64 (m, 2H), 7.66 – 7.84 (dq, *J* = 8.8, 0.8, 0.8, 0.8 Hz, 1H), 7.88 – 8.09 (dd, *J* = 8.8, 1.5 Hz, 1H), 8.22 – 8.51 (m, 2H), 9.95 – 10.30 (d, *J* = 0.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.37, 111.39, 123.36, 125.10, 126.29, 127.62, 130.40, 131.25, 137.09, 137.87, 141.42, 191.58. Otherwise almost rest of the starting material remained unreacted.

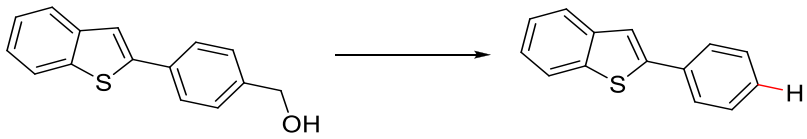


Benzo[b]thiophene (entry 26). Reaction was done by general procedure A for 36 h with benzo[b]thiophen-2-ylmethanol (0.25 mmol, 41 mg), Na_2CO_3 (0.375 mmol, 39 mg), ethylcyclohexane (1mL) and 16 mol% palladium acetate (0.04 mmol, 9 mg) loading. Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Colorless liquid benzo[b]thiophenewas eluted by pet ether only. Isolated yield 60% (20 mg). ^{1}H NMR (400 MHz,

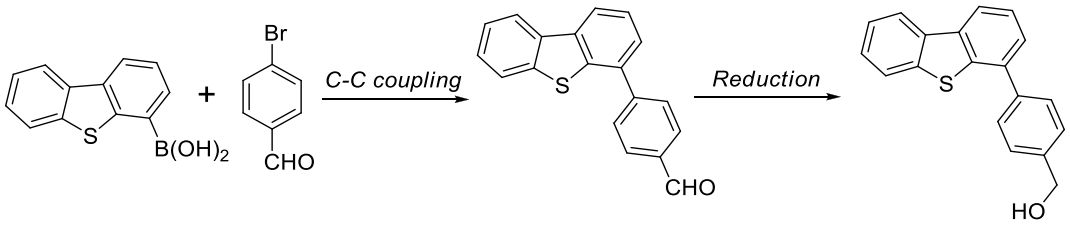
Chloroform-d) δ 7.32 – 7.43 (m, 3H), 7.43 – 7.51 (d, *J* = 5.4 Hz, 1H), 7.81 – 7.88 (m, 1H), 7.88 – 7.96 (ddd, *J* = 7.0, 2.3, 0.9 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 122.68, 123.81, 124.04, 124.34, 124.39, 126.49, 139.76, 139.89. GC–MS (*m/z*): 134.0 $[M]^+$. Otherwise almost rest of the starting material remained unreacted.



(4-(Benzo[b]thiophen-2-yl)phenyl)methanol. C-C coupling was done following general procedure D with benzo[b]thiophen-2-ylboronic acid (1.2 mmol, 214 mg). Reaction mixture was reduced following general procedure B. Yellow crystalline (4-(benzo[b]thiophen-2-yl)phenyl)methanol was isolated through silica gel (60-120 mesh), eluted by pet ether –ethyl acetate mixture (90:10 v/v).Mp: >180 °C.^{1}H NMR (400 MHz, Chloroform-d) δ 4.70 – 4.81 (s, 2H), 7.28 – 7.39 (m, 2H), 7.41 – 7.47 (m, 2H), 7.55 – 7.57 (d, *J* = 0.7 Hz, 1H), 7.70 – 7.74 (m, 2H), 7.76 – 7.80 (m, 1H), 7.81 – 7.85 (m, 1H).

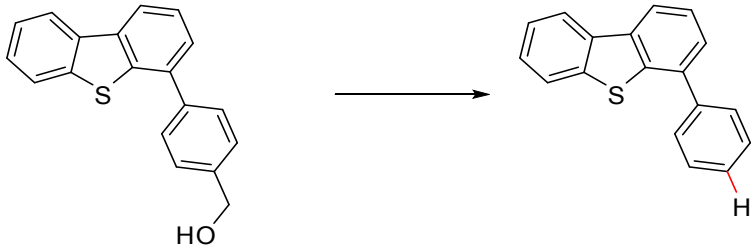


2-Phenylbenzo[b]thiophene (entry 27). Reaction was done by general procedure A for 48 h with benzo[b]thiophen-2-ylmethanol (0.187 mmol, 45 mg), Na_2CO_3 (0.28 mmol, 30 mg), cyclohexane (1mL) and 16 mol% palladium acetate (0.03 mmol, 7 mg) loading. Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 60–120). White solid **2-**Phenylbenzo[b]thiophenewas eluted by pet ether only. Mp: 171-172 °C. Isolated yield 64% (25 mg).^{1}H NMR (400 MHz, Chloroform-d) δ 7.29 – 7.40 (m, 3H), 7.40 – 7.48 (m, 2H), 7.55 – 7.58 (d, *J* = 0.8 Hz, 1H), 7.70 – 7.76 (m, 2H), 7.77 – 7.81 (m, 1H), 7.82 – 7.87 (ddt, *J* = 7.6, 1.5, 0.8, 0.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 119.64, 122.47, 123.76, 124.51, 124.71, 126.68, 128.46, 129.15, 134.47, 139.67, 140.87, 144.42. GC–MS (*m/z*): 210.1 $[M]^+$. Otherwise almost rest of the starting material remained unreacted.

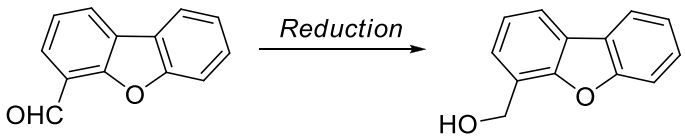


(4-(Dibenzo[b,d]thiophen-4-yl)phenyl)methanol. C-C coupling was done following general procedure D with dibenzo[b,d]thiophen-4-ylboronic acid (1.2 mmol, 272 mg). Reaction mixture was reduced following general procedure B. White crystalline (4-

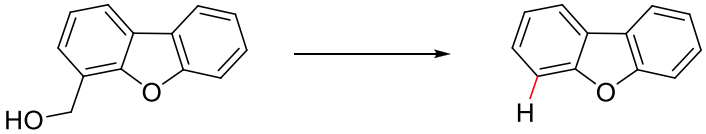
(Dibenzo[b,d]thiophen-4-yl)phenyl)methanol was isolated through silica gel (60-120 mesh), eluted by pet ether –ethyl acetate mixture (85:15 v/v). Mp: 114-115 °C.^{1}H NMR (400 MHz, Chloroform-d) δ 4.74 – 4.89 (d, *J* = 5.2 Hz, 2H), 7.44 – 7.59 (m, 6H), 7.73 – 7.78 (m, 2H), 7.81 – 7.86 (m, 1H), 8.15 – 8.18 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.18 – 8.21 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 65.37, 120.71, 121.95, 122.83, 124.62, 125.33, 127.03, 127.07, 127.64, 128.69, 135.97, 136.45, 136.86, 138.76, 139.73, 140.21, 140.83.



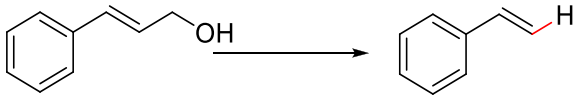
4-Phenyldibenzo[b,d]thiophene (entry 28). Reaction was done by general procedure A for 48 h with (4-(Dibenzo[b,d]thiophen-4-yl)phenyl)methanol (0.20 mmol, 58 mg), Na_2CO_3 (0.3 mmol, 32 mg), cyclohexane (1mL) and 16 mol% palladium acetate (0.032 mmol, 7 mg) loading. Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 60–120). White solid 4-phenyldibenzo[b,d]thiophenewas eluted by pet ether only.Mp: 71-72 °C. Isolated yield 64% (25 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.43 – 7.61 (m, 7H), 7.73 – 7.79 (m, 2H), 7.81 – 7.88 (m, 1H), 8.16 – 8.19 (dd, *J* = 7.8, 1.3 Hz, 1H), 8.19 – 8.23 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 120.65, 121.94, 122.82, 124.58, 125.31, 127.00, 127.11, 128.22, 128.47, 129.01, 135.99, 136.41, 137.23, 138.79, 139.78, 140.80. GC–MS (*m/z*): 260.1 $[M]^{+}$. Otherwise almost rest of the starting material remained unreacted.



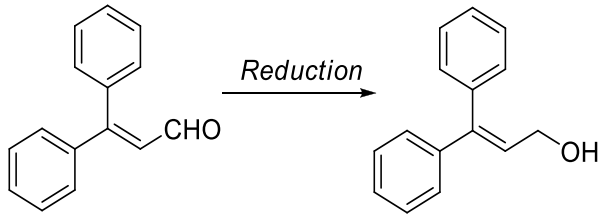
Dibenzo[b,d]furan-4-ylmethanol. Aldehyde was reduced following general procedure B. White solid dibenzo[b,d]furan-4-ylmethanol was isolated through silica gel (60-120 mesh), eluted by pet ether –ethyl acetate mixture (90:10 v/v). Mp: 99°C. ^{1}H NMR (400 MHz, Chloroform-d) δ 2.13 – 2.37 (s, 1H), 5.03 – 5.13 (s, 2H), 7.29 – 7.41 (m, 2H), 7.41 – 7.53 (m, 2H), 7.56 – 7.64 (dt, *J* = 8.3, 0.8, 0.8 Hz, 1H), 7.85 – 7.91 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.92 – 7.99 (ddd, *J* = 7.7, 1.4, 0.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 60.78, 111.95, 120.33, 120.93, 123.04, 123.09, 124.32, 124.44, 124.96, 126.18, 127.42, 154.03, 156.26.



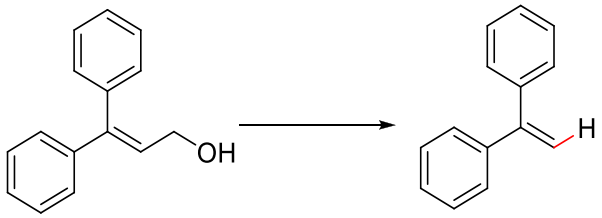
Dibenzo[b,d]furan (entry 29). Reaction was done by general procedure A for 36 h with dibenzo[b,d]furan-4-ylmethanol (0.5 mmol, 99 mg), ethylcyclohexane (2 mL) and 16 mol% palladium acetate (0.08 mmol, 18 mg) loading. Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 60–120). White crystalline dibenzo[b,d]furan was eluted by pet ether only. Isolated yield 65% (54 mg). Mp: 83-85 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.30 – 7.42 (td, *J* = 7.5, 7.4, 1.0 Hz, 2H), 7.42 – 7.53 (m, 2H), 7.54 – 7.64 (dt, *J* = 8.3, 0.8, 0.8 Hz, 2H), 7.88 – 8.05 (ddd, *J* = 7.7, 1.4, 0.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 111.87, 120.86, 122.88, 124.40, 127.33, 156.35. GC–MS (*m/z*): 168.1 $[M]^{+}$. Otherwise almost rest of the starting material remained unreacted.



Styrene (entry 30). Reaction was done by general procedure A with (E)-3-phenylprop-2-en-1-ol (0.5 mmol, 67 mg), cyclohexane (1.3 mL) and 12 mol% palladium acetate (0.06 mmol, 14 mg) loading. Isolated yield 63%. ^{1}H NMR (400 MHz, Chloroform-d) δ 5.30 – 5.49 (dd, *J* = 10.9, 1.0 Hz, 1H), 5.79 – 6.01 (dd, *J* = 17.6, 1.0 Hz, 1H), 6.74 – 6.98 (dd, *J* = 17.6, 10.9 Hz, 1H), 7.36 – 7.42 (m, 1H), 7.42 – 7.51 (m, 2H), 7.52 – 7.66 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 113.93, 126.38, 127.96, 128.68, 137.05, 137.72. GC–MS (*m/z*): 104.0 $[M]^{+}$. Side products detected, ethylbenzene, GC Yield 10%, GC–MS (*m/z*): 106.1 $[M]^{+}$; 3-phenylpropan-1-ol, GC Yield 5%, GC–MS (*m/z*): 136.1 $[M]^{+}$.

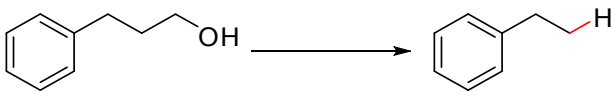


3,3-Diphenylprop-2-en-1-ol. Aldehyde was reduced following general procedure B. Colourless liquid dibenzo[b,d]furan-4-ylmethanol was isolated through silica gel (60-120 mesh), eluted by pet ether –ethyl acetate mixture (90:10 v/v). ^{1}H NMR (400 MHz, Chloroform-d) δ 4.16 – 4.30 (d, *J* = 6.9 Hz, 2H), 6.17 – 6.34 (t, *J* = 6.9, 6.9 Hz, 1H), 7.15 – 7.19 (m, 2H), 7.21 – 7.33 (m, 5H), 7.32 – 7.41 (m, 3H).

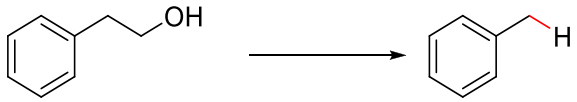


Ethene–1,1–diyldibenzene (entry 31). Reaction was done by general procedure A for 48 h with 3,3-diphenylprop-2-en-1-ol (0.5 mmol, 105 mg), cyclohexane (1.3 mL)

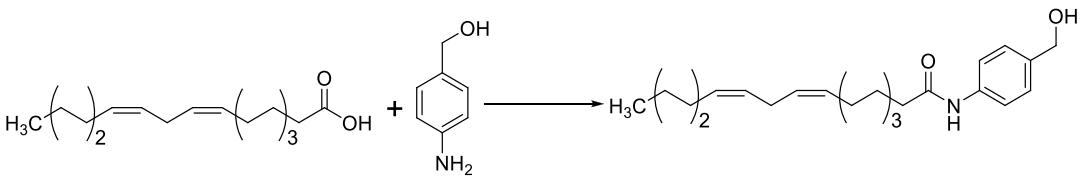
and 16 mol% palladium acetate (0.08 mmol, 18 mg) loading. Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Yellow liquid solid ethene–1,1–diyldibenzenewas eluted by pet ether only. Isolated yield 92% (82 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 5.42 – 5.49 (s, 2H), 7.29 – 7.37 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 114.49, 127.90, 128.36, 128.46, 141.68, 150.24. GC–MS (*m/z*): 180.1 $[M]^+$. Side product detected mixture of homo-coupled product, Isolated Yield 10%, GC–MS (*m/z*): 358.1 $[M]^+$. Otherwise almost rest of the starting material remained unreacted.



Ethylbenzene(entry 32). Reaction was done by general procedure A for 48 h with 3-phenylpropan-1-ol (0.5 mmol, 68 mg) and 16 mol% palladium acetate (0.08 mmol, 18 mg) loading. Yield was determined by gas chromatography. GC yield 52%. GC–MS (*m/z*): 106.1 $[M]^+$. Otherwise almost rest of the starting material remained unreacted.

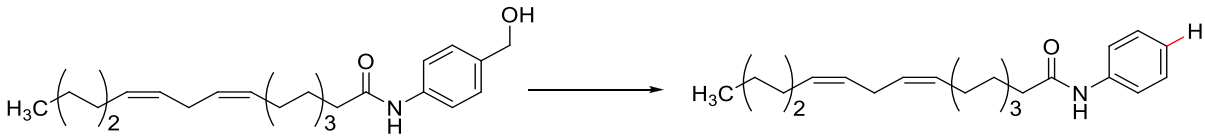


Toluene (entry 33). Reaction was done by general procedure A for 48 h with Phenethyl alcohol (0.25 mmol, 30 mg) and 30 mol% palladium acetate (0.075 mmol, 17 mg) loading. Yield was determined by gas chromatography. GC yield 62%. GC–MS (*m/z*): 92.1 $[M]^+$. Side product detected ethylbenzene, GC Yield 5%, GC–MS (*m/z*): 106.1 $[M]^+$. Otherwise almost rest of the starting material remained unreacted.

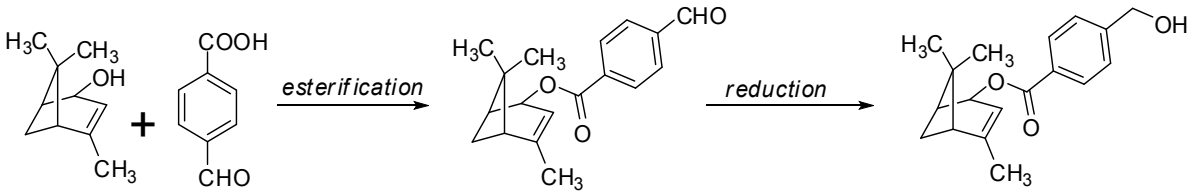


(9Z,12Z)-N-(4-(Hydroxymethyl)phenyl)octadeca-9,12-dienamide.[4] (9Z,12Z)-octadeca-9,12-dienoic acid (Linoleic acid) (2 mmol, 560 mg) was taken in round bottom flask, 5 mL DMF was added to it and was stirred spontaneously at 0ºC. HOBt (1.05 eq., 2.10 mmol, 283 mg), EDC (1.05 eq., 2.10 mmol, 325 mg) was added to it and stirred at 0ºC for 15 mins and more 30 mins at room temperature. (4-Aminophenyl)methanol (2 mmol, 246 mg) was added to it and reaction mixture was stirred at room temperature for overnight. The mixture was diluted with brine solution and extracted with ethyl acetate. Organic part was dried over Na_2SO_4 and concentrated at reduced pressure and product was purified through a silica gel column (mesh 60–120). Yellow solid (9Z,12Z)-N-(4-(Hydroxymethyl)phenyl)octadeca-9,12-dienamide was eluted by pet ether –ethyl acetate mixture (70:30 v/v). Mp: 66-68 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 0.75 – 1.04 (m, 3H), 1.16 – 1.55 (m, 14H), 1.66 – 1.85 (p, *J* = 7.6, 7.6, 7.5, 7.5 Hz, 2H), 1.94 – 2.14 (q, *J* = 7.0, 6.9, 6.9 Hz, 4H), 2.27 – 2.44

(t, *J* = 7.6, 7.6 Hz, 2H), 2.69 – 2.84 (m, 2H), 4.57 – 4.72 (s, 2H), 5.21 – 5.50 (m, 4H), 7.12 – 7.21 (s, 1H), 7.29 – 7.41 (m, 2H), 7.43 – 7.58 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 11.61, 14.27, 22.76, 25.76, 25.81, 27.39, 29.31, 29.42, 29.47, 29.53, 29.79, 31.71, 38.00, 65.14, 120.05, 128.00, 128.07, 128.24, 130.21, 130.42, 136.87, 137.57, 171.54. HRMS (ESI): calcd. for $C_{25}H_{39}NO_2$: 386.3059, found: 386.3067.

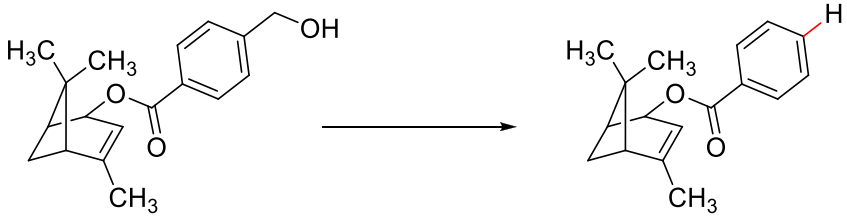


(9Z,12Z)-N-phenyloctadeca-9,12-dienamide (entry 34). Reaction was done by general procedure A for 48 h with (9Z,12Z)-N-(4-(Hydroxymethyl)phenyl)octadeca-9,12-dienamide(0.125 mmol, 48 mg), Na_2CO_3 (1.5 eq., 0.1875 mmol, 20 mg), molecular sieves (35 mg), cyclohexane (1 mL) and 20 mol% palladium acetate (0.025 mmol, 5.6 mg) loading. Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Brown liquid (9Z,12Z)-N-phenyloctadeca-9,12-dienamidewas eluted by pet ether –ethyl acetate mixture (90:10 v/v). Isolated yield 47% (21 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 0.82 – 0.96 (dq,J= 7.4, 3.8, 3.8, 3.1 Hz, 3H), 1.20 – 1.48 (m, 16H), 1.69 – 1.80 (p, *J* = 7.5, 7.5, 7.5, 7.5 Hz, 2H), 1.96 – 2.15 (q, *J* = 6.9, 6.9, 6.9 Hz, 4H), 2.24 – 2.45 (t, *J* = 7.6, 7.6 Hz, 2H), 2.65 – 2.95 (m, 1H), 5.23 – 5.47 (m, 3H), 7.06 – 7.13 (t, J= 7.4, 7.4 Hz, 1H), 7.22 – 7.26 (m, 1H), 7.28 – 7.36 (m, 2H),7.47 – 7.56 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.24, 22.74, 25.80, 27.35, 27.37, 29.29, 29.40, 29.46, 29.51, 29.77, 31.68, 38.00, 119.93, 124.33, 128.07, 128.23, 130.21, 130.40, 136.87, 138.10, 171.58. HRMS (ESI): calcd. for $C_{24}H_{37}NO$: 356.2953, found: 356.2941. Starting material recovered ~25%.

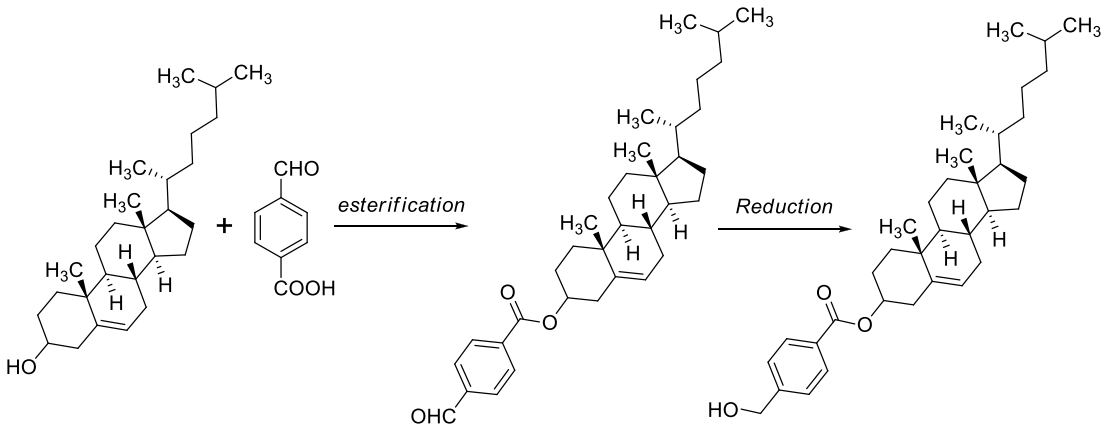


(1S,5S)-4,6,6-trimethylbicyclo[3.1.1]hept-3-en-2-yl 4-(hydroxymethyl)benzoate.4-Formylbenzoic acid (2 mmol, 300mg), Verbenol (2 mmol, 304 mg), DCC (2 mmol, 412 mg), DMAP (2 mmol, 244 mg) and DCM (15 mL) were taken in a round bottom flask and stirred at room temperature for overnight. After reaction mixture was concentrated and corresponding aldehyde was purified through silica gel (100–200 mesh) eluting with pet ether– ethyl acetate mixture (98.5:1.5 v/v). ^{1}H NMR (400 MHz, Chloroform-d) δ 1.13 – 1.21 (s, 3H), 1.34 – 1.45 (s, 3H), 1.47 – 1.53 (d, *J* = 9.1 Hz, 1H), 1.57 – 1.73 (s, 1H), 1.75 – 1.89 (t, *J* = 1.7, 1.7 Hz, 3H), 2.03 – 2.13 (m, 1H), 2.43 – 2.51 (tdd, *J* = 5.9, 5.9, 3.4, 1.8 Hz, 1H), 2.51 – 2.64 (ddd, *J* = 9.2, 6.3, 5.2 Hz, 1H), 5.32 – 5.55 (dp, *J* = 3.1, 1.6, 1.6, 1.6, 1.6 Hz, 1H), 5.68 – 5.97 (dq, *J* = 3.2, 1.8, 1.8, 1.8 Hz, 1H), 7.89 – 8.02 (m, 2H), 8.15 – 8.28 (m, 2H) 9.98 – 10.19 (s, 1H). ^{13}C

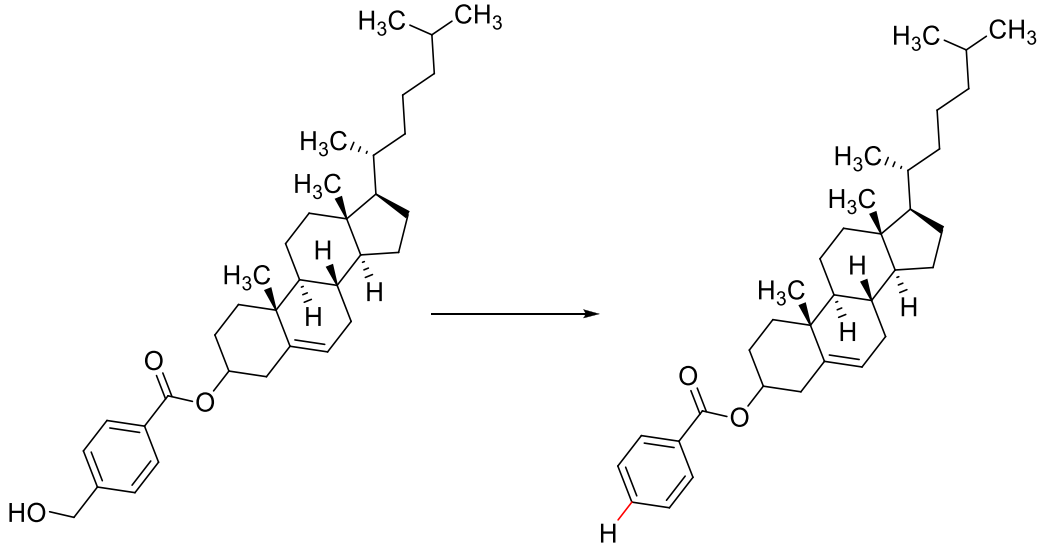
NMR (101 MHz, Chloroform-d) δ 22.98, 23.16, 26.88, 35.87, 40.04, 45.81, 47.85, 76.83, 115.49, 129.71, 130.36, 136.18, 139.17, 150.65, 165.50, 191.96. The aldehyde was reduced following general procedure B.Colourlessliquid (1S,5S)-4,6,6-trimethylbicyclo[3.1.1]hept-3-en-2-yl 4-(hydroxymethyl)benzoate was isolated through silica gel (60-120 mesh), eluted by pet ether –ethyl acetate mixture (98:2 v/v). ^{1}H NMR (400 MHz, Chloroform-d) δ 1.14 – 1.17 (s, 3H), 1.36 – 1.38 (s, 3H), 1.44 – 1.54 (d, *J* = 9.1 Hz, 1H), 1.75 – 1.88 (t, *J* = 1.7, 1.7 Hz, 3H), 2.00 – 2.13 (td, *J* = 5.5, 5.5, 1.3 Hz, 1H), 2.40 – 2.48 (tdd, *J* = 6.0, 6.0, 4.3, 1.8 Hz, 1H), 2.48 – 2.62 (ddd, *J* = 9.1, 6.3, 5.2 Hz, 1H), 4.72 – 4.84 (s, 2H), 5.41 – 5.47 (th, *J* = 3.2, 3.2, 1.7, 1.7, 1.6, 1.6, 1.6 Hz, 1H), 5.71 – 5.82 (tt, *J* = 3.2, 3.2, 1.7, 1.7 Hz, 1H), 7.38 – 7.49 (m, 2H), 7.95 – 8.10 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 22.97, 23.14, 26.92, 35.80, 39.99, 45.85, 47.87, 64.97, 76.05, 115.86, 126.64, 130.05, 130.37, 145.90, 150.12, 166.38. HRMS (ESI): calcd. for $C_{18}H_{22}O_3$: 287.1647, found: 287.1646.



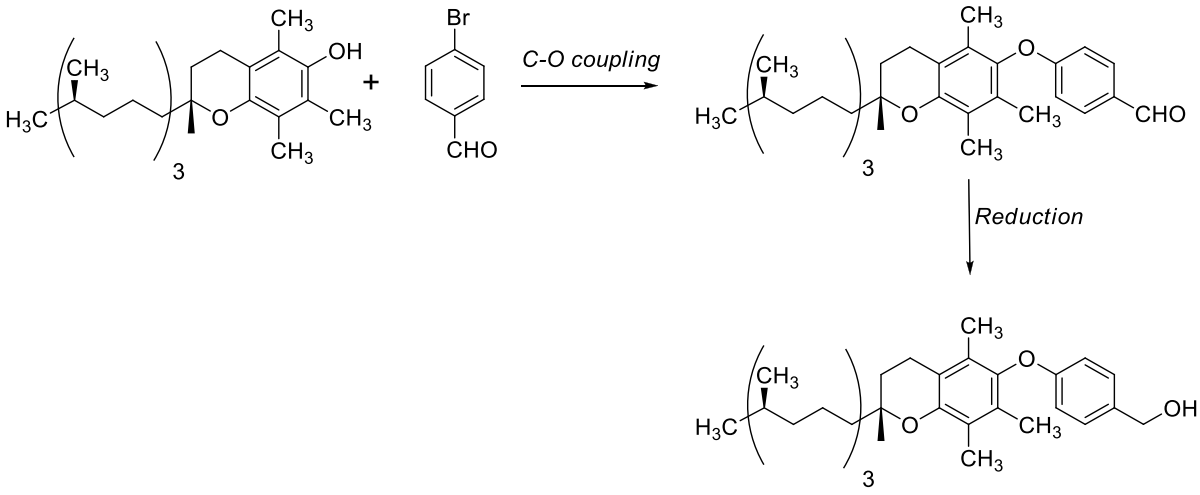
Verbenol benzoate (entry 35). Reaction was done by general procedure A for 48 h with (1S,5S)-4,6,6-trimethylbicyclo[3.1.1]hept-3-en-2-yl 4-(hydroxymethyl)benzoate (0.174 mmol, 50 mg), Na_2CO_3 (1.5 eq., 0.261 mmol, 27 mg), molecular sieves (52 mg), cyclohexane (1 mL) and 20 mol% palladium acetate (0.0349 mmol, 8 mg) loading. Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Colourless thick liquid Verbenol benzoate was eluted by pet ether only. Isolated yield 60% (27 mg).^{1}H NMR (400 MHz, Chloroform-d) δ 1.13 – 1.21 (s, 3H), 1.33 – 1.43 (s, 3H), 1.44 – 1.54 (d, *J* = 9.1 Hz, 1H), 1.68 – 1.86 (t, *J* = 1.8, 1.8 Hz, 3H), 1.97 – 2.21 (m, 1H), 2.32 – 2.48 (m, 1H), 2.49 – 2.64 (dt, *J* = 9.1, 6.0, 6.0 Hz, 1H), 5.35 – 5.50 (s, 1H), 5.70 – 5.94 (s, 1H), 7.36 – 7.48 (t, *J* = 7.5, 7.5 Hz, 2H), 7.47 – 7.62 (t, *J* = 7.4, 7.4 Hz, 1H), 7.94 – 8.14 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 22.97, 23.15, 26.93, 35.80, 40.00, 45.87, 47.89, 76.01, 115.91, 128.44, 128.50, 129.77, 131.17, 132.88, 150.08, 166.55. HRMS (ESI): calcd. for $C_{17}H_{20}O_2$: 257.1542, found: 257.1540. Starting material recovered ~20%.



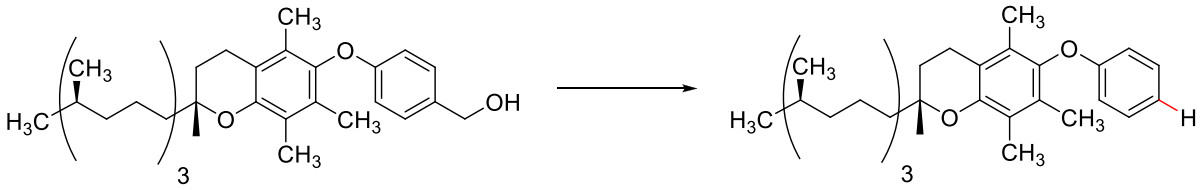
Cholester-3-yl-4-hydroxymethylbenzoate. 4-Formylbenzoic acid (2 mmol, 300mg), cholesterol (2 mmol, 772 mg), DCC (2 mmol, 412 mg), DMAP (2 mmol, 244 mg) and DCM (10 mL) were taken in a round bottom flask and stirred at room temperature for overnight. After reaction mixture was concentrated and corresponding aldehyde was purified through silica gel(100–200 mesh) eluting with pet ether– ethyl acetate mixture (99:1 v/v). White crystalline solid, Mp: 163-166 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 0.62 – 0.74 (s, 3H), 0.80 – 0.89 (d, *J* = 6.7 Hz, 6H), 0.89 – 0.94 (d, *J* = 6.4 Hz, 3H), 0.95 – 2.08 (m, 29H), 2.36 – 2.57 (d, *J* = 8.4 Hz, 2H), 4.76 – 5.01 (dd, *J* = 12.9, 6.7 Hz, 1H), 5.29 – 5.54 (m, 1H), 7.86 – 8.03 (d, *J* = 8.0 Hz, 2H), 8.10 – 8.27 (d, *J* = 8.1 Hz, 2H), 10.05 – 10.13 (s, 1H).^{13}C NMR (101 MHz, Chloroform-d) δ 12.09, 18.94, 19.59, 21.28, 22.79, 23.05, 24.05, 24.51, 28.05, 28.24, 28.45, 32.09, 32.15, 36.02, 36.40, 36.87, 37.21, 38.36, 39.73, 39.94, 42.54, 50.25, 56.35, 56.90, 75.60, 123.26, 129.67, 130.36, 136.05, 139.22, 139.61, 165.17, 191.94. The aldehyde was reduced following general procedure B.White crystalline cholester-3-yl-4-hydroxymethylbenzoate was isolated through silica gel (60-120 mesh), eluted by pet ether –ethyl acetate mixture (98.5:1.5 v/v). Mp: >180 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 0.67 – 0.71 (s, 3H), 0.84 – 0.90 (dd, *J* = 6.7, 1.7 Hz, 6H), 0.90 – 0.95 (d, *J* = 6.5 Hz, 3H), 0.95 – 2.10 (m, 29H), 2.41 – 2.55 (d, *J* = 8.3 Hz, 2H), 4.71 – 4.81 (m, 2H), 4.81 – 4.94 (tt, *J* = 11.7, 11.7, 6.2, 6.2 Hz, 1H), 5.36 – 5.52 (d, *J* = 4.8 Hz, 1H), 7.38 – 7.49 (d, *J* = 8.0 Hz, 2H), 7.94 – 8.14 (d, *J*= 8.0 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 12.09, 18.94, 19.61, 21.27, 22.79, 23.05, 24.05, 24.52, 28.10, 28.24, 28.46, 32.10, 32.16, 36.02, 36.40, 36.88, 37.25, 38.43, 39.74, 39.96, 42.54, 50.26, 56.35, 56.91, 64.98, 74.84, 123.01, 126.60, 130.04, 130.26, 139.86, 145.92, 166.05.



Cholesterol benzoate (entry 36). Reaction was done by general procedure A for 48 h with cholester-3-yl-4-hydroxymethylbenzoate(0.1 mmol, 52 mg), Na_2CO_3 (1.5 eq., 0.15 mmol, 16 mg), molecular sieves (30 mg), cyclohexane (1 mL) and 20 mol% palladium acetate (0.02 mmol, 4.4 mg) loading. Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 60–120). White crystallineCholesterol benzoatewas eluted by pet ether only.Mp: 136-140 °C. Isolated yield 92% (45 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 0.67 – 0.72 (s, 3H), 0.85 – 0.87 (d, *J* = 1.9 Hz, 3H), 0.87 – 0.89 (d, *J* = 1.9 Hz, 3H), 0.90 – 0.95 (d, *J* = 6.5 Hz, 3H), 0.95 – 2.10 (m, 29H), 2.43 – 2.53 (m, 2H), 4.78 – 4.94 (dtd, *J* = 12.3, 8.5, 8.4, 4.5 Hz, 1H), 5.39 – 5.48 (d, *J* = 4.9 Hz, 1H), 7.38 – 7.49 (m, 2H), 7.51 – 7.61 (m, 1H), 7.99 – 8.12 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 12.09, 18.94, 19.61, 21.28, 22.79, 23.05, 24.05, 24.52, 28.10, 28.24, 28.46, 32.10, 32.16, 36.02, 36.40, 36.88, 37.25, 38.43, 39.74, 39.96, 42.54, 50.26, 56.35, 56.91, 74.81, 123.00, 128.47, 129.75, 131.04, 132.93, 139.87, 166.24.



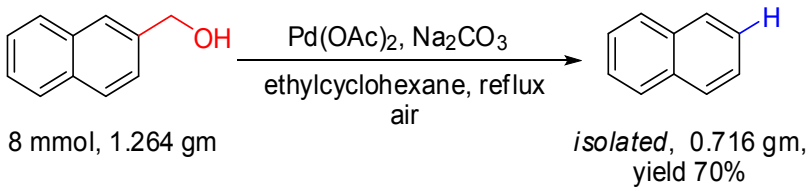
(4-((R)-2,5,7,8-Tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yloxy) phenyl)methanol.[5] 4-Bromobenzaldehyde (2 mmol, 370 mg), $Pd(OAc)_2$ (4 mol%, 0.08 mmol, 18 mg), JhonPhos (6 mol%, 0.12 mmol, 35 mg), K_3PO_4 (2 eq., 2 mmol, 920 mg) were taken in an oven dried schlenk reaction tube, charged with magnetic stir bar. Then the reaction tube was evacuated and back filled with nitrogen. This vacuum/ nitrogen sequence was repeated for four times, (R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl) chroman-6-ol (vitamin E) (2 mmol, 860 mg), Toluene (2 mL) were added under the positive pressure of nitrogen and the resealed tube was immersed in a preheated oil bath at 120 ºC and stirred vigorously for 24 hours. The reaction mixture was cooled to room temperature, diluted with 5 mL ethyl acetate and filtered through celite using additional 10 mL ethyl acetate. The filtrate was concentrated and purified by column chromatography (100–200 mesh) eluting with pet ether– ethyl acetate mixture (99:1 v/v). ^{13}C NMR (101 MHz, Chloroform-d) δ 12.07, 12.17, 13.04, 19.84, 19.91, 19.97, 20.84, 21.25, 22.85, 22.94, 24.08, 24.67, 25.04, 28.20, 31.37, 32.91, 37.63, 37.68, 39.59, 40.22, 75.42, 115.44, 118.32, 123.83, 126.03, 127.88, 130.51, 130.89, 132.36, 133.98, 143.02, 149.41, 164.23, 191.01. HRMS (ESI): calcd. for $C_{36}H_{54}O_3$: 535.4151, found: 535.4151. The aldehyde was reduced following general procedure B.Brown coloured liquid(4-((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yloxy) phenyl)methanol was isolated through silica gel (60-120 mesh), eluted by pet ether –ethyl acetate mixture (98.5:1.5 v/v). ^{1}H NMR (400 MHz, Chloroform-d) δ 0.85–1.04 (m, 12H), 1.06 – 1.77 (m, 24H), 1.78 – 1.97 (ddq, *J* = 20.1, 13.4, 6.8, 6.8, 6.6 Hz, 2H), 2.00 (s, 3H), 2.06 (s, 3H), 2.16 (s, 3H), 2.61 – 2.71 (t, *J* = 6.8, 6.8 Hz, 2H), 4.59 (s, 2H), 6.74 – 6.77 (m, 2H), 7.21 – 7.25 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 12.01, 12.17, 13.04, 19.81, 19.88, 19.95, 20.79, 21.22, 22.83, 22.92, 24.01, 24.62, 25.01, 28.15, 31.44, 32.84, 32.95, 37.47, 37.57, 37.64, 37.74, 39.54, 40.16, 65.04, 75.17, 114.84, 118.01, 123.43, 126.38, 128.29, 128.90, 133.41, 143.47, 148.87, 158.59.



(R)-2,5,7,8-Tetramethyl-6-phenoxy-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman (entry 37). Reaction was done by general procedure A for 48 h with (4-((R)-2,5,7,8-Tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yloxy) phenyl)methanol (0.1 mmol, 53 mg), Na_2CO_3 (1.5 eq., 0.15 mmol, 15 mg), molecular sieves (30 mg), cyclohexane (1 mL) and 50 mol% palladium acetate (0.05 mmol, 11.2 mg) loading. Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 60–120). Colourlessthick liquid (R)-2,5,7,8-Tetramethyl-6-phenoxy-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman was eluted by pet ether only. Isolated yield 68% (34 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 0.84–1.04 (m,

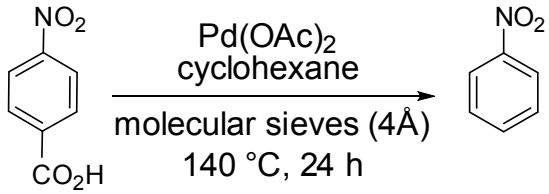
12H), 1.05 – 1.65 (m, 24H), 1.76 – 1.88 (ddq, *J* = 20.1, 13.4, 6.8, 6.8, 6.6 Hz, 2H), 1.96 (s, 3H), 2.00 (s, 3H), 2.11 (s, 3H), 2.58 – 2.62 (t, *J* = 6.8, 6.8 Hz, 2H), 6.73 – 6.75 (m, 2H), 6.90 – 6.92 (m, 1H) 7.20 – 7.24 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 12.04, 12.24, 13.11, 19.84, 19.91, 19.98, 20.85, 21.27, 22.86, 22.96, 24.08, 24.67, 25.05, 28.21, 31.51, 32.90, 33.02, 37.51, 37.58, 37.61, 37.69, 37.79, 39.59, 40.19, 75.21, 114.89, 118.04, 120.98, 123.44, 126.52, 128.44, 129.66, 143.53, 148.89, 159.02. HRMS (ESI): calcd. for $C_{35}H_{54}O_2$: 507.4202, found: 507.4195. Isolated yield of the corresponding aldehyde 4-((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl) chroman-6-yloxy)benzaldehyde is 28%. ^{1}H and ^{13}C NMR spectra were exactly matched with the previous data. Starting material recovered 5%.

Gram scale reaction:



Naphthalen-2-ylmethanol (8 mmol, 1.264 gm),16 mol% palladium acetate (1.28 mmol, 286 mg), Na_2CO_3 (1.5 eq., 12 mmol, 1.260 gm), molecular sieves (2 gm, 4Å) were taken in a 100 mL round bottom flask. Then 15 mL ethylcyclohexane was added to it. Reflux condenser was attached with the round bottom flask and placed on a preheated oil bath at 130ºC. The total reaction mixture was refluxed for 48 h with constant stirring. The reaction mixture was filtered through celite. Pure dehydroxymethylated product was isolated by column chromatography through a silica gel column (mesh 60–120). White crystalline naphthalene was eluted by pet ether only. Isolated yield 70% (0.716 gm).GC–MS (*m/z*): 128.1 $[M]^+$.

Reactions with corresponding acid.

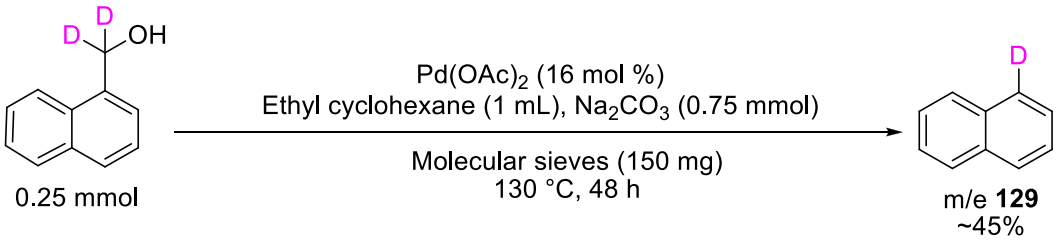


(a) Following **general procedure A**, 4–nitrobenzoic acid (0.5 mmol, 84 mg), 8 mol% palladium acetate (0.04 mmol, 9 mg), 1.3 mL cyclohexane were used. After reaction, mixture was characterized by GC–MS. No trace of nitrobenzenewas found by GC–MS.

(b) Following **general procedure A**, 4–nitrobenzoic acid (0.5 mmol, 84 mg), 8 mol% palladium acetate (0.04 mmol, 9 mg), **K_2CO_3** (0.75 mmol, 104 mg), 1.3 mL

cyclohexane were used. After reaction, mixture was characterized by GC–MS. No trace of nitrobenzenewas found by GC–MS.

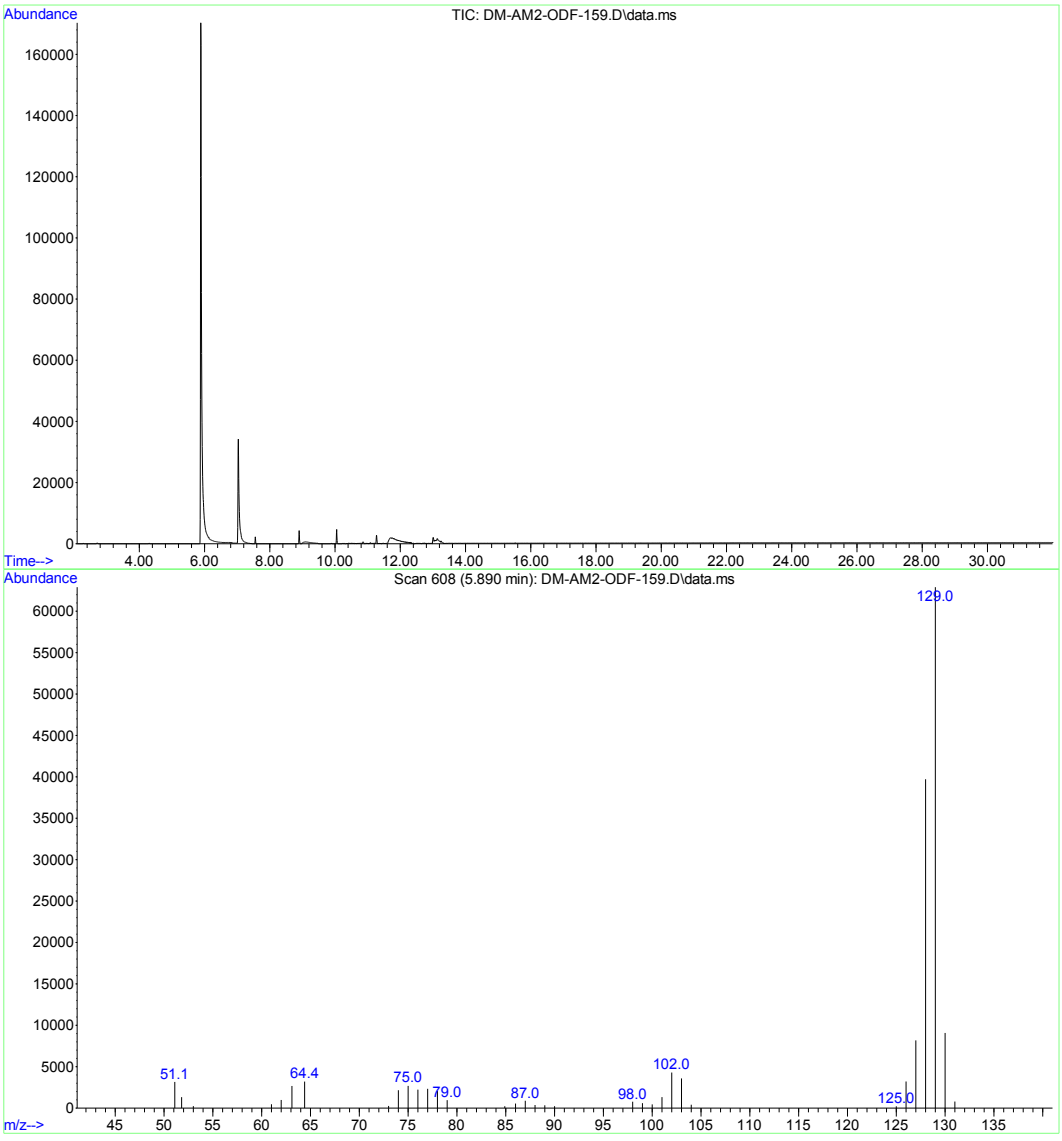
Deuterium labelling experiment:



Reaction was done by general procedure A running for 48 h with naphthalen-2-ylmethanol (0.25 mmol, 40 mg) and 16 mol% palladium acetate (0.04 mmol, 9 mg) loading and ethylcyclohexane as solvent. Pure deformylated product was isolated by column chromatography through a silica gel column (mesh 60–120). White crystalline naphthalene-D was eluted by pet ether only. Isolated yield 45% (14 mg). GC–MS (*m/z*): 129.1 $[M]^+$. Another side product is naphthalene-CD_2H . GC–MS (*m/z*): 144.1 $[M]^+$.

GC-MS spetra of the Deuterium labelling experiment reaction mixture:

File :F:\DM\ATANU MODAK\DM-AM2-ODF-159.D
Operator : ANSHU
Acquired : 26 May 2012 11:22 using AcqMethod ATA.M
Instrument : GCMS
Sample Name: DM-AM2-ODF-159
Misc Info :
Vial Number: 1



File :F:\DM\ATANU MODAK\ODF\DM-AM2-ODF-159.D
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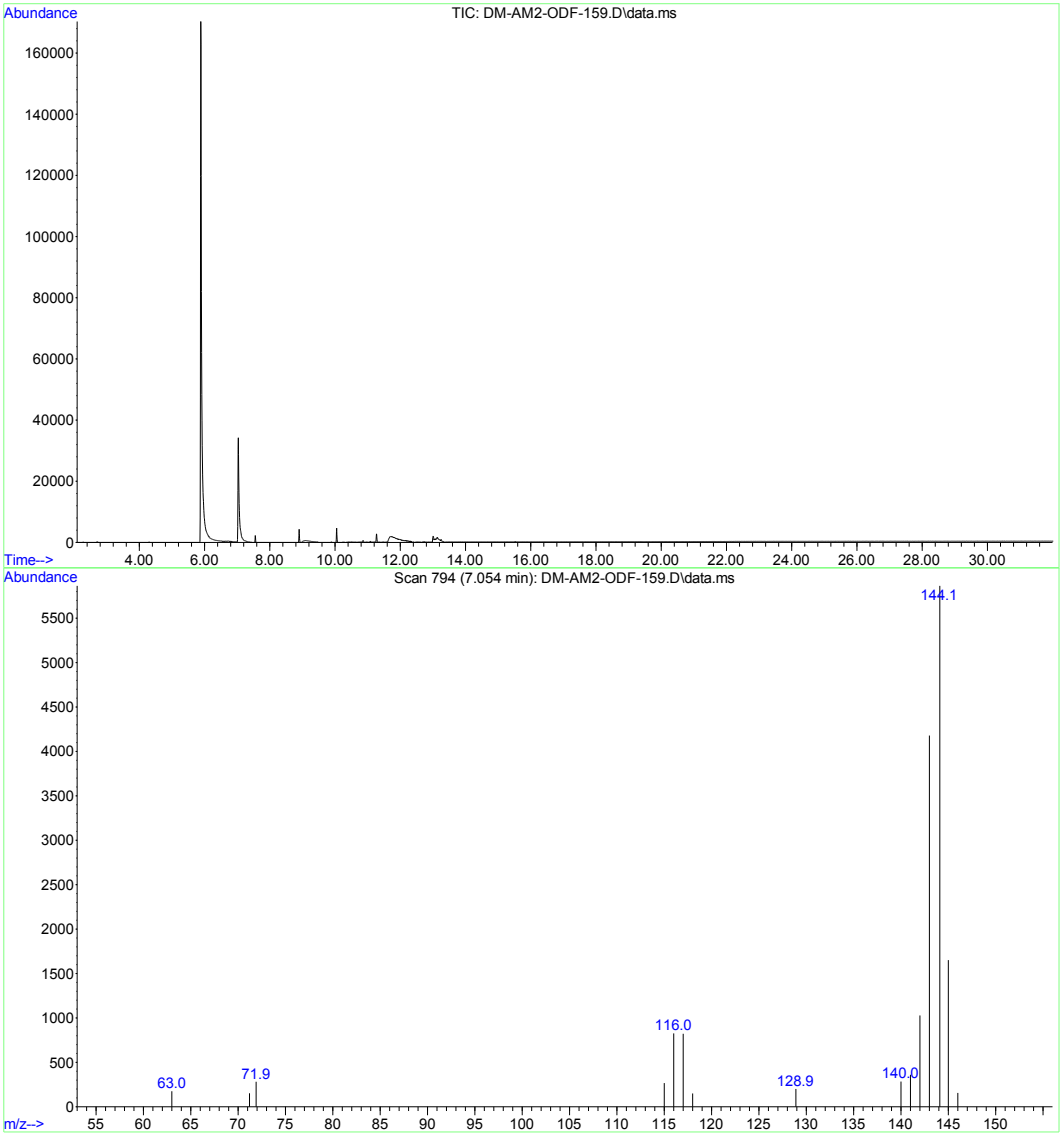
Acquired : 26 May 2012 11:22 using AcqMethod ATA.M
Instrument : GCMS
Sample Name: DM-AM2-ODF-159
Misc Info :
Vial Number: 1



References:

[1]J. C.Antilla, J. M. Baskin, T. E. Barderand S. L. Buchwald, *J. Org. Chem.,*2004, **69**, 5578.

[2]H.N. Nguyen and S.L. Buchwald, *J. Am. Chem.Soc.,*2003,**125**, 11818.

[3]D.Maiti and S.L.Buchwald, *J. Am. Chem.Soc.,*2009,**131**, 17423.

[4]V. Di Marzo, A. Ligresti, E. Morera, M. Nalli, G. Ortar, *Bioorg.Med. Chem*. 2004, **12**, 5161-5169.

[5]L. Salvi,N. R. Davis, S. Z. Ali and S.L.Buchwald, *Org. Lett.,*2012,**14**, 170.